Chapter 1

NTRODUCTION

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Sulfides are often found to be present in the effluents generated from some chemical and petrochemical industries as well as from tanneries. Beyond a certain permissible limit sulfides are generally toxic to living bodies. Sulfur containing compounds such as mercaptans, sulfides and alkali thiosulfates create other major problems like corrosion, odor and toxicity during the designing and repairing of sewer networks [1]. Sodium sulfide, which is a common sulfide bearing material, causes the formation of hydrogen sulfide. Hydrogen sulfide is a major source of air pollution and is related to the problem of acid rain in different parts of the world. Sulfides are often found to be present in industrial wastewater. In some cases it is found in natural waters also. Discharges from a variety of industries such as refineries, petrochemicals, tanneries, kraft paper mills, dyes and pigments often contain substantial quantities of dissolved sulfides. The caustic scrubbing solution from a gas cracker contains sodium sulfide. Sulfides are also found in sewer networks. It primarily originates from anaerobic sulfate respiration in bio-films on sewer pipe walls [2].If there is enough dissolved oxygen available in the downstream, the sulfide gets reconverted to sulfates.

Removal of sulfides from the wastewater coming from industries is a big challenge. Wastewater coming from the refineries, polymer industries and pharmaceutical industries etc are sometimes obnoxious due to the presence of sulfides. Various technologies are used for the removal of the sulfides, which can be divided into the following two main groups [3],

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

1.1 Vapor Phase Technologies

Vapor phase technologies ventilate the point sources of odor problems. This technology is used for the treatment of both air and wastewater. The following technologies work on the principles of vapor phase technologies.

1. Wet scrubbing
2. Liquid redox technology
3. Biofiltration

4. Scavengers
5. Adsorption.

1.1.1 Wet scrubbing

Wet air scrubbing is the most flexible and reliable technology for vapor phase wastewater odor control. 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 in wet scrubbing is purely chemical. One of the major advantages of wet scrubbing systems is the reliability and flexibility provided by the use of chemical reactions. A major challenge in the design and operation of wet air scrubber is the minimization of the usage of chemical and cost while maintaining complete flexible and reliable treatment. The major source of unpleasant smell is hydrogen sulfide which can be removed by adsorption [4].

1.1.2 Liquid redox technology

Liquid redox technology has a relatively long history, but is not widely used to control the odor because of its high capital cost. Liquid redox units use chelated metals dissolved in water solution to remove sulfides from a gas stream and convert it catalytically into solid elemental sulfur. The metal ion in the solution removes electrons (negative charges) from a sulfide ion (S^{-2}) to form sulfur which 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 one due to its is relatively inexpensiveness and nontoxicity. Liquid redox processes have limited applications in wastewater 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 higher, there this technology can be applied economically.

1.1.3 Biofiltration

Biofiltration technology can be used to treat a variety of biodegradable and water soluble contaminants. In a biofilter, the odor contaminants are solubilized from the vapor phase into an aqueous 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 in removing sulfur based odor compounds such as hydrogen sulfide, organic sulfides, inorganic sulfides and mercaptans.

1.1.4 Scavenger

Scavengers 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 system the media is completely consumed. Therefore scavengers are used for low levels of sulfide contaminants.

1.1.5 Adsorption

This system is only applicable for the treatment of the vapor phase stream (air stream). For sulfide removal from wastewater 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 and adhere to the surface of the adsorbent.

1.2 Liquid phase technologies

Liquid phase technologies involve treatment of wastewater 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 wastewater 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.

1. Iron salts method
2. Bio-oxide process
3. Anthraquinone method
4. Oxidizing agents method.

1.2.1 Iron salt method

Iron salts are applied to wastewater to oxidize/precipitate dissolved sulfides. Iron salts such as ferrous salts and ferric salts cause the precipitation of sulfides as ferrous sulfide [5, 6]. Ferric salts such as ferric chloride oxidizes some of the sulfide to sulfur while itself is reduced to ferrous ion. The remaining ferrous iron then reacts with dissolved sulfide to form the ferrous sulfide precipitate. Ferrous sulfide is a light weight precipitate and black in color. It is carried downstream to the treatment plant. With the aeration process of the treatment plant the ferrous sulfide is oxidized to ferric sulfate. The sulfide is oxidized to sulfate and the ferrous ion is oxidized to ferric ion. The ferric ion generated is used for chemical precipitation of phosphorous.

The precipitation method produces sludge of iron sulfides. Iron salts have good catalytic property for the oxidation of sulfides. Ueno et al. [7] made an exhaustive survey of the classical studies on sulfide oxidation. They carried out catalytic oxidation with dissolved oxygen using a number of catalysts including carbon black, ferric salts and a few organic compounds. They worked with synthetic wastewater as well as industrial wastewater. Nielsen et al. [1] reported the effect of $FeCl_3$ catalyst on oxidation of Na_2S with dissolved oxygen. They analyzed the conversion data using a first order rate equation for sulfide removal. The rate constant was found to be a function of $FeCl_3$ concentration.

1.2.2 Bio-oxide process

The bio-oxide process involves the application of nitrate solution of bio-oxide to wastewater. The process uses naturally occurring bacteria to biochemically oxidize the dissolved sulfide. The sulfide typically is either generated upstream of the injection point where no nitrate exists in the wastewater or is contributed downstream via aseptic lateral flow. Nitrate is injected in sufficient quantities to biochemically oxidize the sulfide via the following reaction [8].

$$8NO^-_3 + 5H_2S \rightarrow 5SO_4^{-2} + 4N_2 + 4H_2O + 2H^+$$

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 bio-oxide solution is not classified as a hazardous compound. It is relatively easy and safe to store, handle and apply.

1.2.3 Anthraquinone

Anthraquinone method interrupts the sulfate reduction process carried out by sulfate reduction bacteria in wastewater 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 non-hazardous compound.

1.2.4 Oxidizing agents

Oxidation of wastewater for odor control involves the application of a strong chemical oxidizing agent to the wastewater. The common oxidizing agents are hydrogen peroxide, ozone, permanganate, air and hypochlorites. A common treatment method is wet-air oxidation to sulfates under relatively drastic condition with elevated temperature and pressure [9]. Wet air oxidation is done at an elevated temperature and pressure (160^{o}C, 5 bar) and is a relatively clean process since no solid residue is formed [10, 11]. Air is the naturally available oxidant. It is mostly used as an oxidant with a catalyst. Coal fly ash has been used as a catalyst in the oxidation of aqueous sodium sulfide in the temperature range of 303 to 333K [12]. The deactivation of the catalytic effect of fly ash was found to be less than 31% after the repeated use for five times. The reaction is controlled by both the film diffusion and interparticle diffusion.

Sakai et al. [13] investigated sulfide oxidation by atmospheric oxygen in the presence of "Sulfur Black B" dye as a catalyst. The reaction was reported to follow first order rate kinetics in sulfide concentration.

Biological oxidation of sulfides to sulfates has been used successful only in a limited number of applications [14]. One of the problems of the anaerobic wastewater treatment system is the formation of sulfide by the reduction of the sulfate and other sulfur containing compound. 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 by some researchers [15]. Sulfide oxidation proceeds both biologically and chemically. Biological oxidation in wastewater is typically associated with the activity of colorless sulfur bacteria. These bacteria utilize the energy derived from the following overall reactions.

$$2HS^- + O_2 \rightarrow 2S^\circ + 2OH^- \quad \Delta G^\circ = -169.4 \text{ kJ/mol} \qquad (1)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^- + 2H^+ \quad \Delta G^\circ = - 732.6 \text{ kJ/mol} \qquad (2)$$

Both biological and chemical oxidation is believed to start with the formation of polysulfides which can be protonated to form elemental sulfur. Further oxidation will gives rise to the formation of thiosulfates and sulfates. In order to obtain an effective sulfide oxidation in micro aerobically operated wastewater treatment system sulfide oxidation should be competitive with oxygen for 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.

In many cases it has been observed that the major source of unpleasant smell in wastewater is hydrogen sulfide, which can be removed by wet scrubbing in aqueous sodium hydroxide. The presence of sodium sulfide in wastewater provides a source of hydrogen sulfide. Therefore, complete oxidation of sodium sulfide in wastewater is required to prevent the formation of hydrogen sulfide [4]. Industrial wastewater containing sodium sulfide has often been treated by oxidation method.

In catalytic oxidation process sodium sulfide is oxidized by different catalysts like activated carbon, $FeCl_3$, hydroquinone, 1,4-napthaquinone and 1,4-napthaquinone-2-sulfonic acid [7].

Another way of treating sulfides in wastewater is the oxidation of sulfides by hydrogen peroxide at high pH in the presence of ferrous ion. This process is carried out at ambient temperature [11]. One method of removal of sodium sulfide from wastewater is treating the wastewater with hydrogen peroxide at the freezing point [16]. The reaction is accelerated by freezing. The reaction rate at freezing point was found to be five times faster than that at 25C°.

Sulfur oxides generated by combustion of sulfur containing fossil fuels, such as light gas oil (LGO) cause environmental pollution. Therefore sulfur contents are removed from the petroleum in oil fields and refineries. A classical process used for the sulfur removal is doctor's process in which petroleum is treated with sodium plumbite.The demercaptanizaiton of petroleum distillates can be carried out by sorption of the mercaptan with activated carbon and oxidation of the sorbed mercaptan to disulfide at temperatures between approximately 20^0C to 55^0C [17]. The activated carbon used in the process is commercially readily available. Its surface area typically ranges from between approximately 500 to 1500 m^2 /g and has substantial percentage of the pores in the 10 to 100 A^0 range.

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

1.3 Objective of the Research and Present work

The main objective of the research is to develop safe and efficient methods for the removal of soluble sulfides from waste water. A scan of existing literature [1-78] shows that sulfide was removed by catalytic, photo catalytic and biological oxidation. Biological oxidation can only be used for the limited applications while catalysts used are mostly heavy metals and toxic substance which require complete removal. In the present work we have studied an alternative but largely unexplored processes of Na_2S oxidation. Following methods have been used for the treatment of soluble sulfides in wastewater.

i. Aeration of wastewater in the presence of UV light
ii. Catalytic oxidation of sulfides by hydrogen peroxide
iii. Treatment of sulfides by precipitation using iron salts.
iv. Aeration of sulfidic wastewater in the presence of ultrasonic vibration.

Treatment of both prepared as well as industrial wastewater with sulfide content has been done. Rate equations and activation energies have been calculated in each case. Catalyst used and precipitate formed during precipitation process were characterized by SEM, EDX, FTIR and XRD.

Chapter 2

LITERATURE REVIEW

Water is the vital component of life. It is the best available solvent in the world and is used as a major component in almost each industry [18, 19]. A huge quantity of water is used for different purposes e.g. as solvent and for washing etc in process industries. Therefore the need of treatment of wastewater from industries has been felt for reuse of the water and also get rid of from water related pollution.

Among the wastewater contaminants, sulfide is one of the major contaminants, which not only causes water pollution but also creates air pollution in the form of hydrogen sulfide. Sulfur containing compounds such as mercaptans, sulfides and alkali thiosulfates present major problems like corrosion, odor and toxicity during the designing and repairing of sewer networks. When discharged from the industries, the polluted water can cause water pollution by contaminating water bodies. Due to its corrosive nature, biological removals of hydrogen sulfide processes are being investigated to overcome the chemical and disposal costs associated with existing chemical based removal processes. The nitrogen and sulfur metabolism interacts at various levels of the wastewater treatment process. Hence, the sulfur cycle offers possibilities to integrate nitrogen removal in the treatment process, which needs to be further optimized by appropriate design of the reactor configuration, optimization of performance parameters, retention of biomass and optimization of biomass growth [47].

Oxidation can be done either by chemical or biological methods. Chemical oxidation involves the removal of electrons or addition of oxygen or removal of hydrogen. The available literature on sulfide removal has been divided into three main parts,

(a) Chemical Oxidation
(b) (b) Biological Oxidation
(c) (c) Photo oxidation

2.1 Chemical Oxidation

Nielsen et al. [1] reported the effect of $FeCl_3$ catalyst on oxidation of Na_2S with dissolved oxygen. They analyzed the oxidation data using a first order rate equation for sulfide removal.

The rate constant was found to be a function of $FeCl_3$ concentration. The authors observed that Fe^{+3} reacted slowly with sulfide compared with Fe^{+2} and sulfide precipitation was insignificant. According to their observations an increase in the concentration of Fe^{+3} leads to the requirement of less amount of dissolved oxygen for sulfide oxidation.

In another work Malik et al. [12] reported the effect of coal fly ash as a catalyst on the sulfide oxidation. The effects of coal fly ash loading, source of coal fly ash, speed of agitation, air flow rate and fly ash particle size were studied by the workers. The activity of coal fly ash as a catalyst was found nearly reproducible. The deactivation of catalytic effect of coal fly ash was found less than 31% even after fifth repeated use. The authors concluded that the reaction is controlled by both the film diffusion and inter particle diffusion. They further observed that the mineral phases of coal fly ash are more active than that of unburned carbon present in it towards the catalytic action.

Nielsen et al. [20] further carried out sulfide treatment with ferric chloride and ferrous sulfate salts in sewer wastewater. The author found that sulfide precipitation rate is higher in the presence of ferric chloride salt in combination with ferrous salt. The mechanism of the reaction is explained in the following way in sewer wastewater. Despite its very low solubility iron reacted partly with sulfide and precipitate sulfide to iron sulfide. The addition of ferric salt to anaerobic wastewater can remove sulfides by oxidizing it chemically to elemental sulfur according to Eq(1) while being reduced to Fe^{+2} which can subsequently produce FeS according to Eq (2) .

$$Fe^{2+} + HS^{-} \longrightarrow FeS + H^{+} \qquad (3)$$

$$2Fe^{3+} + HS^{-} \longrightarrow 2Fe^{2+} + S^{0} + H^{+} \qquad (4)$$

When Fe^{+2} is added to anaerobic wastewater containing sulfide it is almost completely converted to ferrous sulfide. On the contrary, if Fe^{+3} is added to aerobic wastewater containing sulfide it is partly converted to iron sulfide. It can be related to the formation of iron bearing complexes in the wastewater. It is not clear from the literature that whether ferric or ferrous iron is more effective in controlling dissolved sulfide concentration.

Tomar and Abdullah [21] reported that a ferric salt solution is slightly more effective than a ferrous salt solution, i.e., the necessary iron dosage for complete sulfide control was 20% lower for the ferric salt solution than the ferrous salt solution. On the other hand, Jameel [22] reported ferrous chloride to be more than twice as effective in controlling the dissolved sulfide concentration compared to ferric chloride. However, field studies indicate that a mixture of ferrous and ferric iron salts is the most effective in controlling the dissolved sulfide concentration [23-25].

Hydrogen peroxide has been used as an oxidant for the oxidation of sulfide both in the presence and absence of catalyst by many workers. One method for the sodium sulfide removal from the wastewater is treatment of sodium sulfide with hydrogen peroxide at relatively high pH in the presence of ferrous ion [26]. This process is carried out at an ambient temperature. In this process different reaction conditions were applied. Five different concentrations of hydrogen peroxide have been applied (0.25ml/liter, 1.5ml/liter, 1ml/liter, 1.5ml/liter, and 2.5/liter). Samples were collected during reaction at 30, 60, 90, 120, 150 180 minutes time intervals after hydrogen peroxide addition. In this oxidation process the main product is sulfate. At a pH of 8.62 sulfide and sulfites present in the wastewater are converted into the sulfates according to the reactions below.

$$S^{-2} + 4H_2O_2 \rightarrow SO4^{-2} + 4H_2O \qquad (5)$$

$$SO_3^{-2} + H_2O_2 \rightarrow SO_4^{-2} + H_2O \qquad (6)$$

$$HSO_3^{-2} + H_2O_2 \rightarrow HSO_4^{-} + H_2O \qquad (7)$$

During this process subsequent decline in the pH was also observed. The use of ferrous ion with hydrogen peroxide produces FeS, which is insoluble. But during this process some hydrogen sulfide is also produced. During this reaction ferrous ion converts into the ferric ion. Ferric ion can remove sulfide by oxidizing it into the elemental sulfur while being reduced itself to the ferrous ion, which produces FeS. The addition of ferrous ion does not have a significant effect on control of odor in wastewater. Because it is oxidized to ferric ion by auto oxidation and results in the formation of elemental colloidal sulfur. The chemical reaction for the oxidation of ferrous ion to ferric ion and formation of FeS and colloidal elemental sulfur are given below.

$$Fe^{+2} + HS^{-} \rightarrow FeS + H^{+} \qquad (8)$$

$$2Fe^{+3} + HS^{-} \rightarrow 2Fe^{+2} + S^{\circ} + H^{+} \qquad (9)$$

Ueno et al. [7] made an exhaustive survey of the classical studies on sulfide oxidation. They carried out catalytic oxidation with dissolved oxygen using a number of catalysts including carbon black, ferric salts and a few organic compounds. They worked with synthetic wastewater as well as industrial wastewater. It was observed that hydroquinone- - $FeCl_3$, $FeCl_3$ - $(NH_4)_2S_2O_8$) and carbon black-Fe_2 $(SO_4)_3$ catalyst systems were very efficient in this regard. The use of $(NH_4)_2S_2O_8$ catalyst was found very useful but because of its poor recoverability as a catalyst in the oxidation with dissolved oxygen makes the process uneconomical. However this catalyst can be useful if rapid and fast oxidation is needed. From economical and technological point of view use of the $FeCl_3$ –Hydroquinone catalyst system is useful for the oxidation with dissolved oxygen.

One method of removal of sodium sulfide from wastewater is treating the wastewater with hydrogen peroxide at the freezing point [16]. The reaction was found to be accelerated by freezing. The reaction rate at freezing point was found to be five times faster than that at 25^0C. The decomposition of sulfide by freezing follow zero-order kinetics, and the rate coefficient was 11.9 mol $liter^{-1}$ min^{-1} at a freezing rate of 0.83-cm^3 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 found to be consumed after 90 minutes of treatment. 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 pH of the solution.

Oxidation has been not only used for the removal of sulfides but also for the removal of the other wastewater contaminants like arsenic and phenolic compounds [27, 28]. In water and wastewater engineering, chemical oxidation serves the purpose of converting putrescible pollutant substances to innocuous or stabilized products [29].

A microbial fuel cell (MFC) has been developed for the removal of sulfur-based pollutants [41]. The fuel cell uses activated carbon cloth and carbon fiber veil composite anode, air breathing dual cathodes and sulfate reducing species. Most the sulfide was electrochemically oxidized to sulfur (polysulfides) by the anode. A small amount of sulfide was oxidized to form higher sulfur oxidation states (oxoanions) that could be reduced again by bacteria to sulfide, only in this case sulfide can be considered as mediator of electron transfer reaction. Elemental sulfur on the anode surface might also be reduced by bacteria. Sulfate and sulfite etc may be produced by bacterial oxidation. The factors that affect the cathode and anode potentials were investigated. Compared with other membrane types, proton (cation) exchange membrane and Nafion ionomer at the catalyst enable the cathode assembly to achieve high performance. The anode performance is controlled by the sulfide concentration. This system might be useful in applications as MFC type biosensor for sulfide determination in wastewater. Sulfur species were nearly completely removed from the wastewater during MFC operation. This approach represents a potential solution for simultaneous electricity production and removal of sulfur-based pollutants (including organic sulfur compounds if they are reducible to sulfide by bacteria), and offers a technological tool both for sustainable energy generation and for economic and efficient removal of sulfur pollutants.

Hydrogen sulfide, a product of sodium sulfide from wastewater can be removed by adsorption [42]. Graphite derived materials modified by incorporation of nitrogen has been used for the removal of hydrogen sulfide. The adsorbent was prepared by spent graphite oxide based materials. Adsorbent was characterized by FTIR, XRD, thermal analysis and potentiometric titration. The removal capacity was found to depend on the dispersion of nitrogen containing species, which is governed by the porosity and structure of the adsorbents. The results of this study showed the formation of new predominantly mesoporous carbonaceous materials in the process of heat treatment of ammonia exposed graphite at high temperatures. Ammonia previously adsorbed on the surface provides nitrogen, which is incorporated to the carbon matrix. Nitrogen enhances the basicity of the adsorbents, contributes to the dissociation of hydrogen sulfide and attracts HS^- ions via electrostatic interactions. Those highly dispersed ions are oxidized to elemental sulfur and, too a much smaller extent, to SO_2. The capacity of the materials in the process of desulfurization is governed by the distribution of those centers and their availability. The latter is affected by the materials structure and porosity. The high volume of mesopores with active chemistry was found to be favorable to hydrogen sulfide reactive adsorption.

Catalytic oxidation of sulfides to sulfoxides using sodium perborate or sodium percarbonate and silica sulfuric acid in the presence of KBr has been done [43,44]. The oxidation generated good yield. Chemoselectivity, the cheapness and availability of the reagents, easy and clean work-up and high yields make this method attractive for chemists.

Oxidation of sulfides to sulfoxides in one-step was conducted by complex catalyst using urea hydrogen peroxide (UHP) in mixture of CH_2Cl_2/CH_3OH (1:1) under air at room temperature [46]. The effect of the reaction conditions on the oxidation of methylphenylsulfide was studied by the workers varying the amount of the catalyst, reaction temperature, reaction time and the amount of UHP. The results showed that using this system in the oxidation of sulfides, sulfoxides were obtained as the main products, together with variable amounts of sulfones (9%), depending on the nature of the substrate. Sulfur dioxide is one of the major source of air pollutant.

In another work sodium sulfide coming from the paper industry has been converted to sodium sulfite which is less hazard than sodium sulfide [52]. The main object of this invention is to provide such a method by which sodium sulfite containing liquor is regenerated and reused and to develop a method of oxidation of sodium sulfide to sodium sulfite. Sodium sulfite is used as the active chemical in a dilute solution of approximately 12% in the semi chemical process but to realize the full benefits of the use of sodium sulfide cooking liquor it is desirable to use a 30% to 35% solution. The pressure during this process was kept above the atmospheric pressure. Such a highly concentrated solution is uneconomical and impractical to use without a successful and economical method of recovering the spent chemicals and regenerating them for repeated reuse. The increased pulp yield is maintained even when the amount of sodium sulfite cooking liquor is double the strength of the reagents employed in other processes. Where more active reagents are used there is no objectionable effect upon the fibers produced. The resulting wood pulp is superior character containing fibers of great strength. The fibers have not been injured by the cooking operation. It is desirable to have an economical recovery and regenerating process which will permit the use and reuse of the sodium sulfite for cooking the wood in the digesters. According to the process mentioned in this invention sodium sulfide is oxidized in an atmosphere of saturated steam and oxidizing gases such as air or oxygen containing gases under controlled conditions of temperature. This conversion is believed to be accomplished by direct oxidation of the sodium sulfide according to the following reaction.

$$Na_2S + 3O \rightarrow 2Na_2SO_3 \qquad (10)$$

Temperature control in this process is important because if temperature goes too high then there will be formation of unwanted sulfates here.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \qquad (11)$$

A process was developed for abating the emission of hydrogen sulfide from a condensate of steam derived from a sulfide containing geothermal brine. It is comprised of introducing an oxidizing agent into the condensate in an amount less than that which would be required to directly oxidize all the sulfide to sulfate [53]. The process optionally provides for periodically introducing a biocide into the condensate to control the growth of organism there. It has been found that the amount of oxidizing agent required to oxidize the sulfides, sulfites and all other oxidizable species present is very small compared to the stoichiometric amount which theoretically would be required. Apparently, some catalytic effect is involved which produces the desired oxidation of the sulfides. Not only is the amount insufficient to oxidize all oxidizable species present in the water, but it is usually far less than that required oxidizing single oxidizable specie. Typically, less than about 10 percent and, generally, less than about 1 percent of the stoichiometric amount of oxidizing agent required to effect substantially complete oxidation of the sulfide and sulfite to sulfate is employed, and preferably for the sulfide alone. In the case of geothermal brines, amounts in the range of about 0.01 percent to about 10.0 percent, and preferably in the range from about 0.2 to 2.0 percent of the stoichiometric amount, have been found to be highly effective. These amounts routinely result in the abatement of at least 50 percent, generally in excess of 80 percent, more often in excess of 90 percent, and mostly about 99 percent of the hydrogen sulfide emissions. Oxidants selected for this process were halogen substituted hydantoins and 1-bromo-3-chloro-5,5-dimethyl-hydantoin and mixture of both.

For water streams which do not contain sufficient sulfide-oxidizing bacteria, such bacteria are incorporated in combination with materials [55]. The rapid-acting sulfide consuming material is selected from the group which includes an iron salt, or a hypochlorite, a permanganate, a persulfate, a perborate, a periodate, a percarbonate, a chlorite, a nitrite, a chlorate, a perchlorate and a peroxide of ammonium, metal or alkali metal and mixtures of these materials. The longer acting chemical which prevents the formation of biogenic sulfide is an ammonium, alkali, alkaline metal, or metal nitrate. Such odors are usually caused by volatile sulfides and other volatile odorous substances. Different composition is provided for controlling odor from wastewater streams. The composition consists of a combination of nitrate salt, sulfide-consuming compound, pH-elevating compound, sulfide-oxidizing, nitrate-reducing bacteria, and sulfide-oxidizing enzyme. In this method a sufficient amount of the composition is added to a waste stream to provide sufficient sulfide-consuming compound to effect immediate removal of sulfide. The composition incorporates a pH elevating compound, which puts the aqueous phase into a pH range where naturally occurring bacteria can more easily metabolize the sulfide. The composition also includes one or more nitrate salts which will accomplish longer term prevention of odors. Specific enzymes are incorporated into the formulation to promote oxidation of sulfide.

Sodium sulfide is used to produce sodium polysulfide and sodium hydroxide by oxidation [54]. Under ideal conditions oxidation proceeds further and results formation of sodium thiosulfate. The oxidation is carried out at or above atmospheric pressure in a mixed reactor or in a pipeline reactor, by sparging oxygen or air, in a mixture of white liquor and lime mud particles produced in the recausticizing plant of a kraft mill. The main objective of this invention was to produce kraft pulping liquor by the oxidation of white liquor in the presence of lime mud. White liquor contains sodium sulfide which is oxidized to sodium thiosulfate and is reused. In this process of regenerating sodium hydroxide from aqueous solution of sodium sulfide consists of heating aqueous sodium sulfide in the presence of metal selected from the group consisting of iron, cobalt and mixtures of these for a time and at a temperature sufficient to form metal sulfide, sodium hydroxide and molecular hydrogen. The metals which can be utilized to desulfurize aqueous sodium sulfide include iron, cobalt or other effective metals which will yield a metal sulfide and sodium hydroxide when reacted with sodium sulfide, and mixtures of these. In accordance with the instant invention, sodium sulfide solutions were heated in the presence of a metal capable of forming a metal sulfide. The heating was conducted for a time and at a temperature sufficient to cause the metal to react with the sulfide solution and yield sodium hydroxide, metal sulfide and hydrogen. Heating temperatures may range from 380^0C to about 425^0C preferably 400^0C to about 425^0C and heating times from about 30 minutes to about 2 hours. The selectivity and conversion of sodium hydroxide is directly proportional to the surface area of the metal. The larger the surface area of the metal, the higher the conversion and selectivity to NaOH. Therefore, the metal will preferably have a particle size of 38 to about 1200 µm. More preferably the metal will have a particle size of about 50 to 150µm. Most preferably, a metal powder will be utilized in the instant invention. The stoichiometry dictates that at least 1 mole iron must exist for every 2 moles of sodium sulfide. Once the NaOH has been regenerated, it can be easily harvested by methods known to those skilled in the art. For example, the hydrogen produced during the regeneration can simply be removed followed by NaOH removal [59].

In this work for the oxidation of sodium sulfide anthracite has been used as catalyst which has high efficiency and low cost. Anthracite is known as smokeless coal and is generally used as a filter. The catalyst occurs in nature and is not expensive.Its activity as a catalyst is same as activated carbon. Further, anthracite is insoluble in alkali and it causes no contamination with an organic substance such as quinine or phenolic substance and no trouble such as foaming as well.

A method for oxidizing sulfide in a viscous aqueous solution of a hydratable polymeric material suitable for use in hydraulically treating subterranean formations was developed by Brown [57]. The hydratable polymeric material consists of polysaccharides, polysaccharide derivatives, polyacrylamides, polyacrylamide polymers and mixtures of all these. Hydrogen peroxide was used as an oxidant. pH was kept between 3 to 10 during the treatment process. Hydratable polymeric materials are frequently used in subterranean formations to increase the viscosity of aqueous solutions, particularly in petroleum production operations such as well completion, fracturing and water flood operations, either to prevent the premature loss of the hydraulic liquid, or to assist in suspending solid particles in the liquid. Such solid particles may be used as propping agents in a fracture; the solid particles may also be used to form either an impervious consolidated pack in contact with a formation to seal off a porous formation or a permeable pack to retain solid particles within unconsolidated formation. Subterranean formations suitable for treatment by the method of the present invention may often be those which are accessible by a borehole into the earth. However, the method is equally suitable for use with more accessible formations where anaerobic conditions may exist. A wide variety of hydratable polymeric materials has been found useful as thickening agents in such aqueous compositions. These include hydratable polysaccharides, polyacrylamides, and polyacrylamide copolymers. Particularly desirable polysaccharides include galactomannan gums and cellulose derivatives.

Typical polysaccharides include guar gums, locust bean gum, karagya gum, sodium carboxymethyl guar, hydroxyethyl guar, hydroxypropyl guar, sodium hydroxymethyl cellulose, sodium carboxymethyl-hydroxyethyl cellulose, and hydroxyethyl cellulose. Optionally, cross-linking agents may be added which increase the maximum temperature at which the hydratable polymers will retain the desired high viscosity. These cross-linking agents include polyvalent metal ions, such as chromium (III), aluminum (III), titanium (IV) and polyvalent anions, such as borates. The viscosity of aqueous solutions formulated with such hydratable polymeric materials can be reduced or broken by the use of chemical additive "breakers", such as enzymes, acids and strong oxidizing agents. Per sulfates and activated per oxygen compounds are frequently used as breaking agents because they readily form effective free radicals under the usual conditions of use and leave no objectionable residue to cause disposal problems.

A method of treating an aqueous sodium sulfide solution such as white liquor in kraft pulping systems for oxidation of the sulfide with oxygen in the presence of a specific activated carbon catalyst such as particulate activated carbon catalyst having an average particle diameter of 0.2-4 mm, a pore volume of at least 0.25 cm^3/g in pores with diameters of not smaller than 100 ^0A and a pore volume of at least 35% of the total pore volume in pores with diameters of not smaller than $100A^0$ or a fibrous activated carbon catalyst having a specific surface area of 300-2500 m^2/g and an outer surface area of 0.1-5 m^2/g was established. In this process the aqueous solution is passed through a bed of granular solids to filter out the suspended solids and filtrate obtained containing sodium sulfide is free of suspended solids. The oxygen containing gas and filtrate are passed concurrently in the presence of activated carbon catalyst. The reaction results formation of polysulfide or sodium hydroxide in solution. Oxygen containing gas is fed from the middle portion of the bed of activated carbon catalyst with the remainder oxygen containing gas being fed from the top. The activated carbon catalyst is separated into two or more vertically spaced a part layers and wherein a dispersing plate having a multiplicity of openings is disposed between each of the adjacent two layers, the total area of said openings of each dispersing plate being 15-35% of the area of said dispersing plate. Bulk density of fibrous catalyst was 0.027-0.126 cm^3/g. The temperature was kept between 50 to 130^0C and the pressure was from 0 to10kg/cm^2.The feed ratio of containing gas to filtrate was maintained 10-500. This process has high importance. It not only get ride us from the sulfide which is harmful to the environment if left without treatment but also make the kraft pulping process economical.

In the kraft pulping process, it is known to be effective to use a cooking liquor containing polysulfide for the digestion of wood [58]. In such a pulping system it is indispensable to treat the spent cooking liquor and to prepare polysulfide-containing cooking liquor there from. Thus, the spent liquor, which is called black liquor, is concentrated and combusted. The melt of inorganic chemicals, which is called smelt, obtained as a residue from this combustion is dissolved to form green liquor essentially consisting of sodium carbonate, sodium thiosulfate and sodium sulfide. The sodium carbonate is then converted into sodium hydroxide by causticizing.

A process of converting sulfide ion present in a solution to save water soluble sulfur species (sulfates) was developed by Allison [60]. The present invention is related generally to processes for converting sulfide ion to innocuous, water soluble sulfur species, and more particularly, but not by way of limitation, to a process for oxidizing sulfide ion present in solutions containing hydrogen sulfide to sulfate ion. The process basically consists of mixing surface active agents with sulfide ion to inhibit formation of elemental sulfur and to facilitate conversion of sulfide to sulfate. The sulfide ion can be oxidized to water soluble sulfur species by contacting the sulfide ion with an oxidizing agent for a period of time sufficient to convert the sulfide ion to sulfate ion. For this process suitable surface active agents are those selected from the group consisting of polyoxyalkylene alkylphenols, polyoxyalkylene alcohols, and metal salts of alkylbenzene sulfonic acids, alkyl ether sulfates, and quaternary amines. To enhance formation of sulfate ion as opposed to elemental sulfur and to speed up the reaction, the pH of the reaction mixture can be adjusted to a level greater than7. For this process the oxidizing agents used are chlorine, hypochlorite, hydrogen peroxide, chlorine dioxode, sulfur dioxide, ozone and compounds containing a nitrogen-chlorine bond. The process provided increases water flooding capabilities and makes disposal of the emerging waters easier to handle and environmentally safe.

A process for the synthesis of polysulfides from the sulfides by oxidation was developed by Mehrer [61]. Polysulfides are used in the pulping industry. This process is not only capable of removing sulfide but also produces the polysulfides which is used in the pulping industry.In this process polysulfides were prepared from the sodium sulfide by oxidation in the presence of transition metal oxide catalyst (MnO_2). The consumption rate of oxygen was atleast $1.5x10^{-4}$ moles.sec. The process of present invention was carried out in a self recirculated reator.

A process in which sulfite pulping chemical is produced by exothermic oxidation of sodium sulfide was developed by Shick [62]. The heat evolved during exothermic reaction was used to make the steam. This steam was then mixed with the air and was used for the oxidation process. The temperature in the reactor was controlled adiabatically.

Sulfide can be used for the removal of molybdenum, arsenic and silicon by precipitation [64]. A method was developed for removing arsenic, molybdenum and Silicon from the tungstate solution. Removal was affected by the addition of sulfuric acid with the sulfide. The removal exceeds 95% while the loss of tungsten during purification amounted to about 3%. Zinc was removed from the Bayer process liquors by sodium sulfide. It was an inexpensive process compared to the other processes of zinc removal from the Bayer process liquor. In this process zinc is precipitated as zinc sulfide. The analysis was done by Atomic absorption spectrophotometer.

The metal ferrite (chromium ferrite and zinc ferrite) sorbents made from the heavy metals wastewater sludge have been developed for the hydrogen sulfide removal from caol gas [66]. Hydrogen sulfide was removed from coal gas by metal ferrite in a fixed bed reactor. Metal ferrites in powder form were the products of ferrite process for the heavy metal removal from the wastewater. Porosity analysis results shows that number of micropores of the sorbents were decreased .The optimum temperature range was between 500 to 600^0C. Effects of various concentrations of H_2 and CO were also conducted at different temperatures. By increasing the H_2 concentration, the sulfur sorption capacity of the sorbent decreases and an adverse result is observed in the case of increasing CO concentration. The XRD scan shows that the FeS, ZnS, and MnS peaks are observed on the sulfided sorbents.

Mathematical modeling is used to study the sulfide removal by Santos and Lopes [67]. Different processes for the hydrogen sulfide removal from wastewater by oxidation has been studies. Four different empirical expressions have been compared during the treatment in an aerated biofilter. The importance of this removal process has been recognized by an emission model. Out of four models two were able to predict the mean of hydrogen sulfide removed fraction within a confidence interval of 95% and they demonstrated good agreement with the experimental data. Biodegradation and oxidation were the two main mechanisms in the biofilter where as stripping and volatization made only minor contributions.

Kinetics study explains the factors which affects the rate of reaction. Kinetics of oxidation of sulfide based biofilter slag reactor was studied by Uvarovskii [68]. Kinetics of sulfur dioxide formation as well as changes in slag mass at 1073 to 1173 K was studied. The optimal temperature range of sulfide slag oxidation was 1173 to 1223K.The conversion of sulfate was 96%. Mathematical modeling suggests sulfur dioxide and sulfate formation.

Hydrogen sulfide has been removed from the sour gas and has been converted into hydrogen and sulfur at low temperatures [49]. The anodic oxidation of sulfide ions, formed by scrubbing sour gas with sodium hydroxide at a pH of nearly 14, produced polysulfide ions. The cathodic product was hydrogen, with the electrolyte in the cathode chamber being NaOH. The electrolyte in the anodic and the cathodic compartments was separated by an ion exchange membrane (Nafion). The sodium polysulfide was transferred to a separate chamber through which sour gas, at a high concentration (I0-15 vol %) of H_2S, was passed through it. Crystalline sulfur was produced by this reaction. The filtrate was mixed with the solution obtained by hydrogen sulfide scrubbing and returned to the electrolytic cell. Extremely pure hydrogen and sulfur were produced at a low cell voltage ($E_{cell} = 1.0$ V), and at a high current density (i = 300 mA cm^{-2}). The absorption of hydrogen sulfide in sodium hydroxide has been tested. The removal of hydrogen sulfide is complete at high rates for NaOH concentrations more than 2 M. The precipitation of sulfur is out of the cell. Pure sulfur is produced on passing H_2S, CO_2 and oxygen containing gas through the solutions at room temperature.

Method of analysis of sulfide in colored water was developed using ion chromatography [51]. Its principle is based on the complete oxidation of sulfide into sulfate by hydrogen peroxide. The difference between samples analyzed before and after this treatment gives the total dissolved sulfide. In order to avoid H_2S exhaust this oxidation needs to be performed immediately after sampling without cell separation. Standard solutions were prepared using raw anaerobic effluents from an industrial plant. There was no bacterial culture in the wastewater samples. This method cannot be used with accuracy because of the chance of incomplete oxidation of sulfide. Oxidation of sulfide by hydrogen peroxide in the absence of catalyst is slow.

The most modern and more accurate methods of sulfide analysis are iodometric titration and methylene blue methods [11, 26]. Oxidation is an important and useful process for the treatment of sulfur bearing waste materials. It has not only importance in the wastewater treatment but it is also used in the purification of crude oil.

The catalytic properties of acids, metal compounds, and carbonyl compounds in reactions of oxidation of medium-sulfur crude diesel cut sulfides with hydrogen peroxide are examined by Sharipov [45]. Comparative data on the effectiveness of these catalysts have been reported. The mechanisms of formation of sulfoxides and sulfones with these catalysts have been described. The possible mechanism of the effect of the catalysts has been discussed. Optimum reactor designs which ensure minimal residence time of diesel cut sulfides in the reaction zone with effective heat and mass exchange have been described.

A hydrazone Schiff base-Fe^{+3} complex using salicylidene benzoyl hydrazine (L) as ligand has been synthesized and characterized by elemental analyses, IR, NMR and UV–Vis spectroscopy. Hydrogen sulfide can be removed electrochemically from the sour gas at ambient temperature [73]. The method was studied by varying initial hydrogen sulfide concentration, temperature, flow rate of the gas component of gas mixture and current density. Hydrogen sulfide removal increases by increasing temperature and current density. On increasing the initial sulfide concentration and gas flow rate decrease in the percentage of hydrogen sulfide removal was observed.

Heavy metals were removed from wastewater by precipitation with sodium sulfide [72]. The reaction was carried out on the surface of bentonite. This method approximately removed 90% Cd as CdS from $CdCl_2$ solution. Additional reactions are related to the removal of excess sodium sulfide by the release of hydrogen sulfide and oxidation to sulfur using carbogen gas (5% CO_2 and 95% O_2) followed by aeration. It is very much clear that most of the sulfide removal from the wastewaters and waste gases require substantial amount of energy inputs.

An electrochemical method was presented here by means of a fuel cell that removes sulfide and produce energy [71]. A laboratory scale fuel cell was operated at ambient temperature and neutral pH which has not only removed sulfur but also generated power. Potassium ferricyanide was used as cathodic electron acceptor. Elemental sulfur was identified as the predominant final oxidation product that was deposited on the anode. The elemental sulfur deposited on the anode should be removed after three months because it made limit the operation of fuel cell. The presence of organic compounds did not affect this process. Elemental sulfur is the major final product of the electrochemical oxidation of sulfide. A maximum power of 166 w/m^3 was obtained and the power generation depends upon on the amount of sulfide in the liquid stream.

2.2 Biological Oxidation

Biological oxidation of sulfides to sulfates has been used successful only in a limited number of applications [15]. The bad odor of the wastewater results from hydrogen sulfide which is mostly generated from sodium sulfide. Sodium sulfide on reaction with carbon dioxide and sulfur dioxide forms hydrogen sulfide.Hydrogen sulfide is also produced if sodium sulfide solution becomes neutral or acidic. Hydrogen sulfide can be removed from wastewater by different methods such as wet scrubbing and biological oxidation.

Biological oxidation in combination with denitrification has been used successfully for the removal of sulfides. Sulfide to sulfate oxidation, with nitrate as a terminal electron acceptor, proved to be very successful. An incoming concentration of 110mg S^{-2}/liter was found to be totaliterlitery converted to SO_4^{-2}. At complete denitrification, the concentration of S^{-2} in the reactor effluent was less than 0.1 mg/L [30]. As hydrogen sulfide is a toxic and corrosive gas it causes environmental and economic problems in a variety of sectors such as sewage, oil fields, petrochemical industry etc. Nitrate method has been demonstrated by different researchers to be very effective in controlling and removing sulfides from wastewater [31-32].

Sulfide and organic carbon can be removed in the presence of nitrate and nitrite [48]. An anaerobic attached growth bioreactor was operated for 510 days to treat sulfide laden organic wastewater where nitrate and nitrite are introduced as electron acceptors. This simultaneous autotrophic and heterotrophic desulfurization–denitrification process has provided a demonstration of the possibility to eliminate sulfide and organic carbon in the presence of nitrate and nitrite. It was observed that sulfide was removed up to 100% in the anaerobic attached growth bioreactor when influent sulfide loading rate ranged from 115.9 to 1800mg/liter.

Simultaneous removal of sulfide and nitrate were carried out in the anaerobic reactor under shock loading [76]. The effect of shock loading is directly proportional to the intensity of shock loads. The reactor performance was found stable at relatively lower intensity of the shock loads. The performance was able to recover from disturbances at all the tested shock loads. In 30h, all the performance indices of the reactor could return to the initial stable state. The recovery velocities of the indices were constant, which changed with the intensity of shock loads.

A microbial consortium attached onto a polyethylene was used to evaluate the simultaneous oxidation of sulfide and phenol by denitrification [77]. Phenol, sulfide and nitrate were loaded into fluidized bed reactor. It was found that under steady state conditions the consumption efficiency is 100%. The phenol and sulfide loading rates applied to the reactor did not affect the denitrification process.

Denitrifying bacteria can grow on a wide range of substrates, however, many of these are too expensive to be economically usable for wastewater treatment. A number of colorless sulfur bacteria are capable of anaerobic growth, if nitrate or nitrite serves as an electron acceptor. The group includes several obligate autotrophes, such as T. denitrificans and Thiomicrospira (Tms.) denitrificans [34-36].

An expanded granular sludge bed (EGSB) reactor was adopted to incubate bio-granules that could simultaneously convert 4.8 kg.S m^{-3} d^{-1} of sulfide in 97% efficiency; 2.6 kg-N m^{-3} d^{-1} of nitrate in 92% efficiency; and 2.7 kg-C m^{-3} d^{-1} acetate in 95% efficiency [36]. Mass balance calculation of sulfur, nitrogen, and carbon over the EGSB reactor confirmed the performance results of the bacteria. This noted reactor performance was found to be much higher than those reported in literature. Stoichiometric relation suggests that the nitrate was reduced to nitrite via autotrophic denitrification pathway and then the formed nitrite was converted via heterotrophic denitrification pathway to N_2. Problem with biological oxidation of sulfide lies in its limited applications and cost factor particularly in a case of big continuous wastewater treatment processes. Introduction of a limited amount of oxygen to anaerobic bioreactors is proposed as a simple technique to lower the level of sulfide in the biogas.

Van et al. [15] has explained the results of a bioreactor study and of batch experiments that were performed to obtain better insight into the state of sulfur compounds and oxygen during micro-aerobic sulfide oxidation. The authors observed that the introduction of a low airflow (0.7–0.9 m^3 m^{-3} d^{-1}), corresponding to an O_2/S molar ratio of 8–10) to a fluidized bed reactor fed with low-sulfate vinasse was sufficient to reduce the biogas H_2S-content to an undetectable level. Sulfide was initially oxidized to elemental sulfur, thiosulfate and most probably to polysulfide. Significant sulfate production did not occur.

A bioreactor packed with chitosan was developed to treat a liquid stream of sulfide [2]. The sulfide removal efficiency was about 100% when the volumetric loading was increased from 3.9mmol S.liter^{-1}.h^{-1} with a space velocity of 72h^{-1}. When the aeration was increased from 0.05 to 0.1 l/min the average removal efficiency improved from 81 to 94%. A removal efficiency of 90% was obtained after 15 days of operation with a load rate of 8.9 mmols/dm^3.h and a space velocity of 14.28h^{-1}.

In another process hydrogen sulfide has been removed by biofiltration [63]. The operation was carried out at 40, 50, 60 and 70^{0}C using microbial community obtained from a hot spring. In this process three biotrickling filter (BTF) systems were set up in parallel for a continuous run of 9 months to operate at three different temperatures, one of which was always at 40°C as a mesophilic control and the other two were for exploring high temperature operation up to 70°C. From the experiments it is clear that addition of glucose and monosodium glutamate enhanced thermophilic biofiltration of hydrogen sulfide gas and a removal rate. In this process glucose acts as a carbon source for the existing microbial community in the biotrickling filtration while glutamate is acting as a Compatible solute. This work clearly shows that biological gas cleaning of hydrogen sulfide can be conducted at temperatures up to 70°C and opens up the prospects for applying this technology for a wider range of emissions at high temperature.

A biological process has been developed to clean off-gases containing sulfur dioxide from industrial installations [47]. In this process sulfur dioxide is converted into elemental sulfur which can be reused or can be easily separated. Sulfide and other sulfur compounds are removed from the crude oil in refineries and oil fields.

Hydrogen sulfide has been removed by bench scale cross flow horizenatl biotrickling filter by Duan [70]. Sulfide oxidizing bacteria were obtained from the activated sludge. The performance of horizontal biotrickling filter was evaluated systematically over 120 days by changing the following factors.(i) Inlet hydrogen sulfide concentration (ii)Gas retention time (iii)pH of the recirculation solution (iv) pressure drop and (v) shocking load. Activated carbon in this system acts as an organism carrier. A preliminary investigation into the different effects of bacterial biodegradation and carbon adsorption on system performance was also conducted.

The kinetic study of heterogenous reaction between dissolved sodium sulfide and biologically produced sulfur particles has been studied by measuring the formation of polysulfide ion at pH of 8.0 and temperature of 30-50^{0}C [70]. This study has big importance in the biotechnological removal of hydrogen sulfide. The data was fitted with a reaction rate model in which heterogenous reaction kinetics, decreasing particle size and a non-uniform particle size distribution were incorporated. Polysulfide ion formed in this reaction has autocatalytic effect. The small particle size or the specific hydrophilic surface properties probably make the surface of the biologically produced sulfur particles more easily available for reaction than the surface of granular sulfur.

Sulfide oxidation by nitrate in the presence of phenol was investigated by Cardoso and Texie [50]. The authors examined the effect of initial sulfide concentration on the kinetics and metabolism of phenol and sulfide in batch using nitrate as electron acceptor. Complete oxidation of sulfide (20 mg liter^{-1} of S^{-2}) and phenol (19.6 mg liter^{-1}) was linked to nitrate reduction when nitrate was supplemented at stoichiometric concentrations. At 32 mg liter^{-1} of sulfide, oxidation of sulfide and phenol by the organo–lithoautotrophic microbial culture was sequential; first sulfide was rapidly oxidized to elemental sulfur and afterwards to sulfate; phenol oxidation started once sulfate production reached a maximum. When the initial sulfide concentration was increased from 20 to 26 and finally to 32 mg liter^{-1}, sulfide oxidation was inhibited. In contrast phenol consumption by the denitrifying culture was not affected. These results indicated that sulfide affected strongly the sulfide oxidation rate and nitrate reduction.

During the biological treatment of wastewater sulfate reducing bacteria cause the formation of hydrogen sulfide. It was found that hydrogen sulfide formation can be inhibited by the addition of magnesium oxide [74]. It was also found that magnesium oxide inhibits the sulfide formation by reducing the number of sulfate reducing bacteria. The experimental results showed that magnesium oxide is able to inhibit biogenic sulfide and the number of sulfate reducing bacteria, sulfide concentration and the sulfate reducing rate were decreased. The concentration of sulfide in the wastewater during biological treatment showed the abundance of sulfate reducing bacteria. Different concentrations of magnesium oxide were added to the wastewater during biological treatment. It was found that sulfide concentration and sulfate reducing bacteria decreased by increasing the concentration of magnesium oxide.

2.3 Photo Oxidation

Oxidation of sodium sulfide in the presence of UV light has also been done by many workers. The process is known as photo oxidation of sulfide. Photo oxidation has been studied by many workers both in the presence and absence of catalyst [29, 37, 38, 39, and 40]. In the presence of catalyst photo oxidation is not economically suitable for large continuous wastewater treatment processes. A 60w germicidal lamp was applied as a light source [40]. UV light intensity measurements were performed by using IL 1700 research photometer. To perform photo oxidation of sodium sulfide at different intensities a variable transformer was used to adjust the power input to the UV light. Sulfide was found to produce hydrogen and sulfur by UV light treatment. Sodium sulfide solutions were illuminated with ultraviolet light (λ = 253.7 nm) to produce hydrogen and disulfide ion in equimolar amounts. Elemental sulfur could be recovered from the disulfide solution via purging with H_2S and then filtering. The resulting filtrate was also found to be photoactive, suggesting the possibility of a continuous closed cycle photochemical operation for H_2S decomposition into its constituent elements. The production of hydrogen depends upon on the intensity of incident light and concentration of sulfide.

Photo oxidation of sodium sulfide in the presence of polynuclear phthalocyanine complexes as a catalyst has also been studied [39]. The water soluble zinc and aluminium complexes and the metal free derivative of tetrasulfophthalocyanine were employed as sensitizers for the photo oxidation of sodium sulfide under irradiation with visible light in oxygen saturated aqueous alkaline solution in the presence of oppositely charged latexes or detergents. Detergents strongly increase the photo activity of sensitizer. Latexes also increase the photo activity of sensitizer and simultaneously the photo degradation of sensitizer.

Chapter 3

MATERIAL AND METHODOLOGY

In the present work oxidation of sodium sulfide has been carried out by air in the presence of UV light, catalytic oxidation by hydrogen peroxide, precipitation using iron salts followed by aeration and aeration in the presence of ultrasonic vibration. The aeration of wastewater containing sulfide has been carried out in the presence of different intensities of UV light. During the aeration process following variable has been changed.

1. Air flow rate
2. Oxygen concentration
3. Sulfide concentration
4. UV light intensity. Kinetics of this process was investigated by changing the following parameters.

(a) Sulfide concentration

(b) Oxygen concentration in the air

The rate equation has been determined from the experimental data. During the oxidation process sulfide was oxidized to sulfate. Sulfide was analyzed by UV-visible spectrophotometer using methylene blue method. Sulfate was analyzed by UV-visible spectrophotometer after addition of $BaCl_2$ reagent. Both Synthetic and industrial samples were treated.

The catalytic oxidation of sodium sulfide has been carried out using ferric oxide catalyst. The catalyst has been prepared in the laboratory from ammonia and ferric chloride. It was then characterized by SEM, EDX, FTIR, TGA and XRD. The oxidation was carried out in the glass vessel. Sodium sulfide solution, catalyst and hydrogen peroxide were stirred during the process using magnetic stirrer. Oxidation process was studied by changing the following parameters.

I. Sulfide concentration

II. Amount of hydrogen peroxide

III. Amount of catalyst

IV. Temperature.

Rate equation and activation energy were calculated from the experimental data. Both synthetic and industrial wastewaters were treated.

Sodium sulfide from the wastewater has been removed by using iron salts. Both industrial and synthetic samples were treated. Incase of industrial wastewater residual sulfide concentration is removed by aeration. During aeration the process was studied by changing the air flow rate. The precipitation process was studied by changing the following parameters.

a. Fe^{+3}/Fe^{+2} ratio

b. Initial sulfide concentration

c. Temperature.

Rate equation and activation energy were calculated from the experimental data. The precipitate formed was characterized by SEM, EDX, XRD, and FT-IR

Aeration of sulfidic wastewater was carried out in the presence of ultrasonic vibration. Sodium sulfide oxidized to elemental sulfur and pH of the solution increases slightly from the initial value. The process was studied by varying the following variables.

(i) Initial sulfide concentration

(ii) Air flow rate

(iii) Ultrasonic vibration frequency.

Rate equation has been determined from the experimental data.

3.1 Photo-Oxidation of Sodium Sulfide

Photo oxidation of sodium sulfide was carried out by sulfonated phthalocyanines in oxygen saturated aqueous solution containing detergents or latexes by Spiller et al [38]. In the present work sodium sulfide was oxidized by air in the presence of UV light. The oxidation was investigated by using different air flow rates, oxygen concentration, sodium sulfide concentration and UV light intensities. Figure-1 shows an experimental setup to demonstrate the process of removing sulfide ions from a solution. The reactor is comprised of a glass vessel (1), a UV emitting lamp (2), a dissolved oxygen (DO) probe (3), a pH probe (4), a sparger (5) for distributing air and said solution taken in the reactor. The UV emitting lamp (2) was connected to power supply (9). This experiment was used to emulate the actual implementation of the same process on wastewater, whereby oxidation of sodium sulfide in wastewater (1) to sodium sulfate occurs. It is to be noted that the DO probe (3) was dipped into the liquid (1) in the apparatus only to measure the dissolved oxygen concentration, and the pH probe (4) monitored the pH of the solution. In this investigation we have followed new method of sulfide oxidation in aerated aqueous solution by exposure to UV radiation. The UV emitting lamp (2) used in the application was placed inside a tube made of quartz in order to transmit UV radiation from the source without absorption in the wall. This type of arrangement was chosen to create the most efficient UV emission and absorption capability.

The quartz tube used not only allowed UV radiation to pass through effectively, but also protected the UV lamp (2) from the solution when the UV lamp (2) and tube (6) was submerged into solution containing sulfide (7). Besides the UV lamp (2) and quartz tube (6), the dissolved oxygen (DO) probe (3) and pH probe (4) were also dipped into the solution inside the glass reactor (1) in order to measure the concentration of DO and pH of said solution throughout the whole process. Another apparatus that was submerged into the liquid in the glass reactor is a sparger (5), which was comprised of an opening at one end and at least one perforation to the other parts of the sparger (5) to allow air to flow into the reaction (8). In this setup, the perforated openings were submerged in the solution, allowing atmospheric air (8) to flow through the opening, which was not submerged in the solution and to flow to the perforated openings, creating air bubbles in the solution. This method will dissolve the atmospheric air into the sulfide solution. The experiment was done using four initial concentrations of sulfides: 500mg/liter and 700mg/liter, 1000mg/liter and 1300mg/liter at fixed air flow rate of 4 liter/min. Different oxygen concentrations were used at constant air flow rate of 4 liter/min, at constant initial sulfide concentration of 700ppm and constant UV light intensity of 4 watts. Different UV light intensities were used at constant air flow rate of 4 liter/min, constant initial sulfide concentration of 700 ppm and constant oxygen concentration of 21%.Oxidation of sulfides were investigated by using different air flow rates 1liter/min,2liter/min,4 liter/min,6 liter/min and 8 liter/min at constant initial sulfide concentration of 700ppm, constant UV light intensity of 4watts and constant oxygen concentration of 21%. The concentration of sulfides dropped over time while the concentration of sulfates increased over time. The final concentration of sulfates was approximately the same as the initial concentration of sulfides in the solution. Figure-2 shows a schematic diagram of a multi-compartment device for UV lamp intensity of 4 watts.

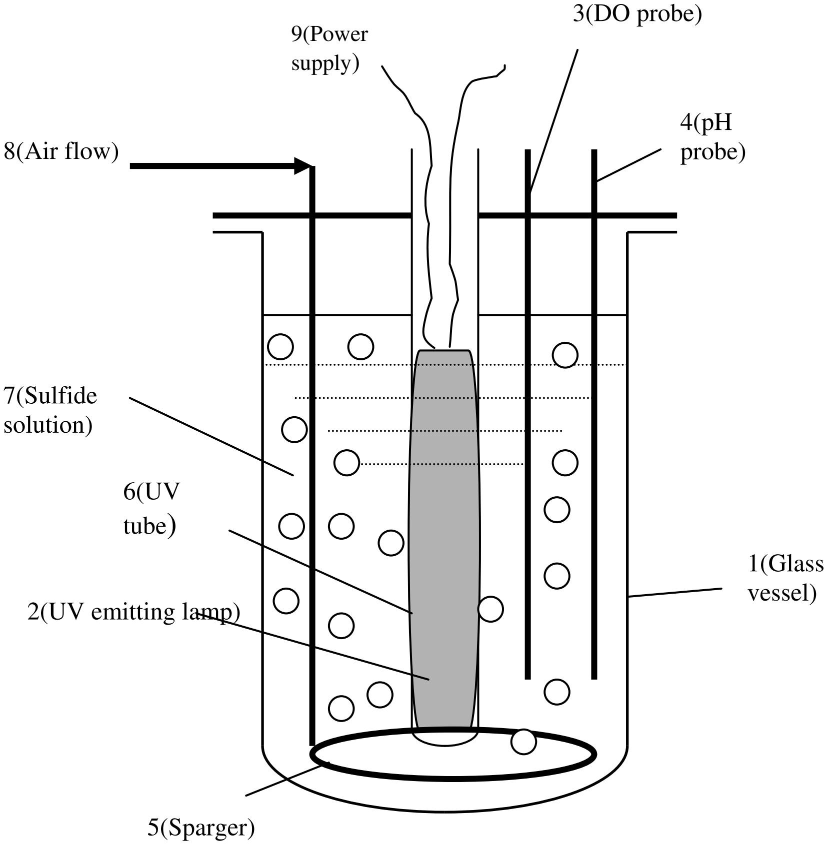


Figure-1: Schematic diagram of the reactor for the photo oxidation of sulfide.

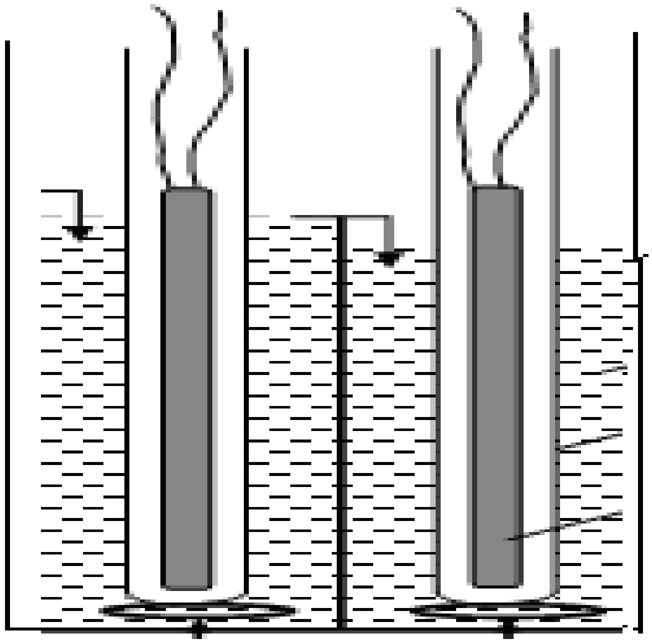


Figure-2: Schematic diagram of a multi compartment device for UV light photo oxidation of sulfide.

3.2 Catalytic oxidation of sodium sulfide by hydrogen peroxide

3. 2.1 Preparation of catalyst

Analytical grade ferric chloride was taken as the starting material for the synthesis of ferric oxide catalyst. 30% ammonia solution was added drop wise to a concentrated solution of ferric chloride with stirring till the pH became 8.5. The slurry was washed repeatedly with water to remove excess chloride ions and then dried in an air oven at 110±5°C, powdered and stored. The catalyst was characterized by FT-IR, XRD, SEM and EDX. FT-IR analysis of the catalyst was carried out with Perkin-Elmer apparatus (Model number = Spectrum one). The XRD analysis of the catalytic sample was carried out with BRUKER apparatus (Model number =D8 ADVANCE). SEM and EDX analysis of the catalytic sample was carried out with LEO apparatus (Model number = 1430 VP).

3. 2.2 Procedure of the catalytic oxidation process

Removal of sulfides from wastewater by hydrogen peroxide at freezing point has been done in the polypropylene syringe by Takenaka et al [16]. In this process Sodium sulfide has been taken in the polypropylene syringe and hydrogen peroxide has been put into the polypropylene syringe by micro syringe. Polypropylene syringe contains a mixture of sodium sulfide and hydrogen peroxide. It has been immediately transferred to a thermostat for freezing purposes. Reaction was also carried out at room temperature. Rate of decomposition of hydrogen peroxide was found 47 times faster at freezing point than at room temperature.

In the present work the oxidation of sulfide by hydrogen peroxide was carried out in the presence of ferric oxide catalyst. The catalytic oxidation was carried out in a stirred vessel. During the process pH, dissolved oxygen and temperature were measured using Hach pH meter, Hach dissolved oxygen meter and thermometer respectively. Different dosages of catalyst were added to 500 ml sulfide solution followed by addition of H_2O_2 in different proportions. Samples were withdrawn from time to time and analyzed for the unreacted sulfide and sulfate formed. The oxidation process was also investigated at different initial sulfide concentrations. The temperature effect on oxidation process was checked by carrying out the process in a water jacketed glass reactor at four different temperatures. The whole experimental setup has been shown in Figure-3.

3. 3 Precipitation of sulfides using iron salts

Tomar and Abdullah [21] has carried out sulfidic waste water treatment with ferric salt solution. And it was found slightly more effective than a ferrous salt solution, i.e., the necessary iron dosage for complete sulfide control was 20% lower for the ferric salt solution than the ferrous salt solution. On the other hand, Jameel [22] reported ferrous chloride to be more than twice as effective in controlling the dissolved sulfide concentration compared to ferric chloride.

In this study solution of sodium sulfide was taken in a water jacketed glass reactor and a mixture of hepta hydrated ferrous sulfate and anhydrous ferric chloride solutions were added to it with stirring. Stoichiometric amount of iron (iron required for precipitate formation) was added in each case in the form of Fe^{+2} and Fe^{+3}salts. The color of the liquid changes and precipitate formation starts. Samples of the solution were taken from time to time and were analyzed for the sulfide. In case of high concentrated sulfidic wastewater the residual sulfide was removed by aeration of the system (precipitate and residual sulfide). Sulfate formation due to reaction of sulfide with air during aeration could not be measured since the excess sulfate from the added reagents was already present in the solution. pH was measured using Hach pH meter. The precipitate formed was characterized by FT-IR, XRD, SEM and EDX. FT-IR analysis of the precipitate was carried out with Perkin-Elmer apparatus (Model number = Spectrum one). The XRD analysis of the precipitate sample was carried out with BRUKER apparatus (Model number =D8 ADVANCE). SEM and EDX analysis of the precipitate sample was carried out with LEO apparatus (Model number = 1430 VP).The experimental set up has been shown in Figure-4.

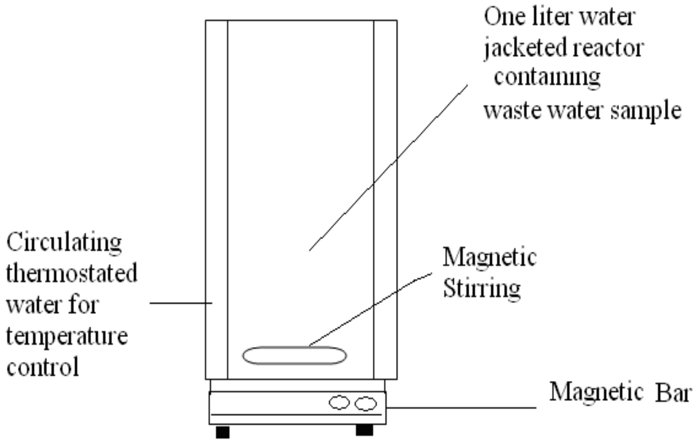


Figure-3: Schematic diagram of the set up for catalytic oxidation of sulfide

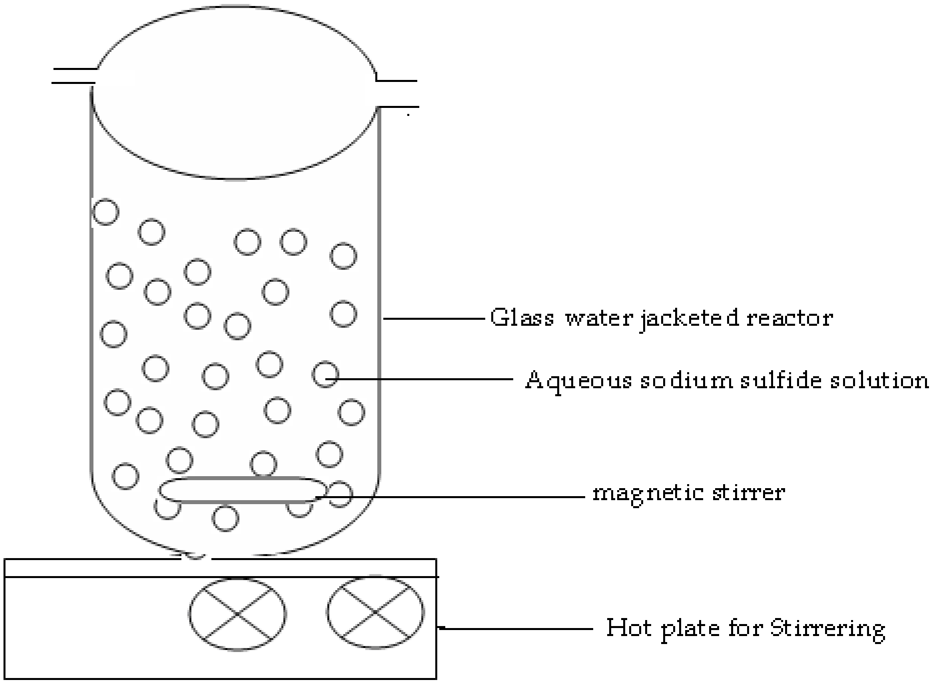


Figure-4: Schematic diagram of the set up for precipitation of sulfide.

3.4 Aeration of sulfide in the presence of ultrasonic vibration

Sodium sulfide was oxidized by air in the presence of ultrasonic vibration. The oxidation was investigated by using different air flow rates, sodium sulfide concentration and ultrasonic vibration. Schematic diagram of the process is shown below. Figure-5 showed an experimental setup to demonstrate the process of removing sulfide ions from a solution. The reactor was comprised of a glass reactor, ultrasonic vibrator, dissolved oxygen (DO) probe and sparger for distributing air in the solution taken in the reactor. The ultrasonic vibrator was connected to power supply. The DO probe was dipped into the liquid in the apparatus only to measure the dissolved oxygen concentration, and the pH probe monitored the pH of the solution. The glass reactor was dipped in the water inside the ultrasonic vibrator. We cannot use ultrasonic vibrator as a reactor because in that case the temperature of the solution raises. The ultrasonic vibration was transferred into the solution inside the reactor by water present in the ultrasonic vibrator. Before the sulfide analysis carbon disulfide was added in order to dissolve the elemental sulfur formed during the oxidation.

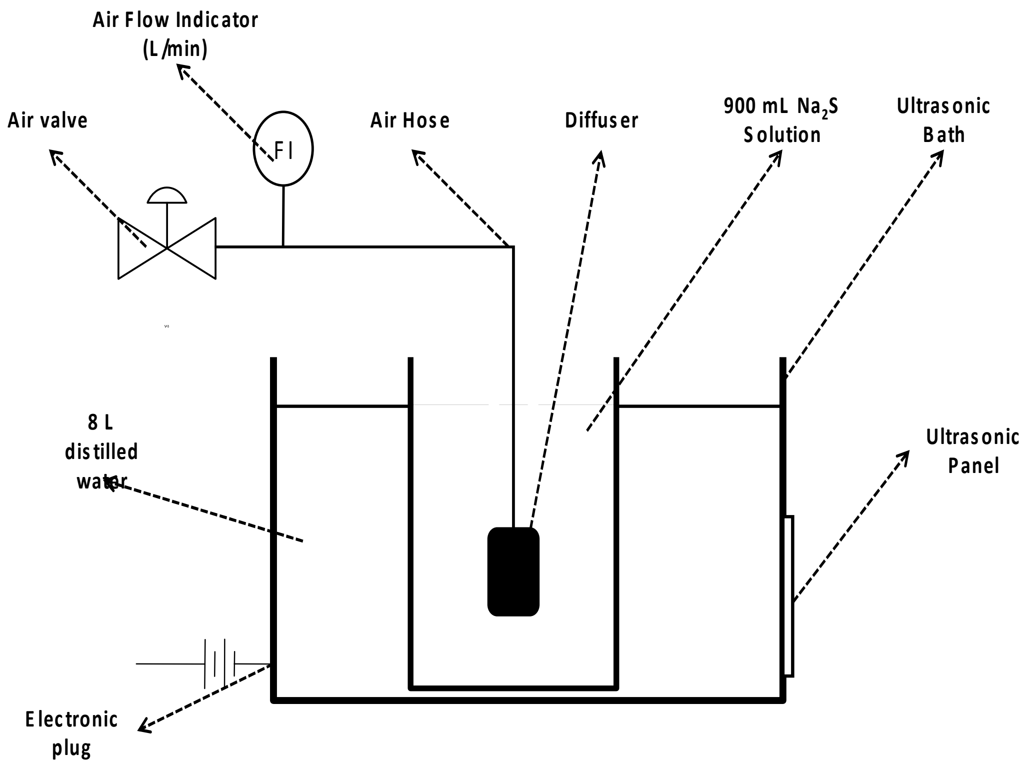


Figure.5: Schematic diagram of the aeration in the presence of ultrasonic vibration

Chapter 4

RESULTS AND DISCUSSION

4.1 Photo aeration of sodium sulfide

Oxidation of sodium sulfide was carried out by air in the presence of UV light. The process was investigated at different initial sulfide concentrations, different air flow rates, different oxygen partial pressures and at different UV light intensities. Experimental data of photo aeration in tabulated form has been given in the appendix (table-1 to table-14). It was found that oxidation of sulfide proceeds through the formation of thiosulfate and eventually leading to the formation of the end product sulfate. Initial pH of the sulfide solution was 12 or more depending upon the sulfide concentration. It was found that as oxidation of sulfide to thiosulfate and eventually to sulfate continues, the pH of the solution reduces gradually with an ultimate value very near to 7 which is neutral pH. A solution of the ultimate oxidation product, sodium sulfate, was found neutral having pH nearly 7. Oxidation of 500 ppm of sulfide takes 40 minutes. The rate of oxidation is higher at high initial concentration of sulfide. With the increase in the initial concentration of sulfide the time of oxidation of sulfide increases. It was found that oxidation of 1300 ppm of sulfide takes nearly 170 minutes. The airflow rate and UV light intensity used were fixed at 4l/min and 4watts respectively. From the experiment as done with the experimental setup and process as shown in Fig 2, the concentration of sulfides dropped over time while the concentration of sulfates increased with time. Photo oxidation of sulfide at different initial sulfide concentrations has been shown in Figure-6.

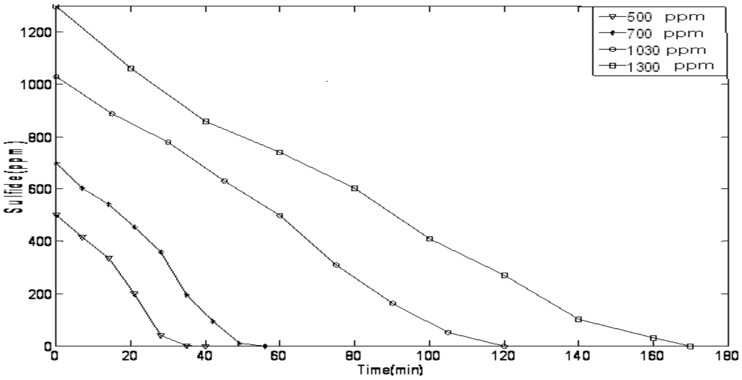


Figure-6: Relationship between sulfide concentration and time in photo oxidation

The final concentration of sulfates is approximately the same as the initial concentration of sulfides in the liquid. From this experiment, it is clear that the process of removing sulfide ions from wastewater by means of reaction between photo-excited sulfide ion and dissolved oxygen in wastewater is quite effective. The concentration of final product of sulfide oxidation (sulfate) is higher at high concentration of sulfide. The rate of formation of sulfate is higher at high concentration of sulfide. Sulfate formation during oxidation reaction at different initial sulfide concentrations has been shown in the Figure-7.

In Figure-8, change in the pH and dissolved oxygen concentration has been shown. The experiment was done using an initial sulfide concentration of 700mg/liter, airflow rate of 4liter/min and UV light intensity of 4 watts. It was found that the amount of dissolved oxygen was constant during the oxidation while the pH of the liquid decreased over time. This is because during bubbling of air, the oxygen from the air gets dissolved in the solution and the dissolved oxygen reacts with photo-excited sulfide ions.

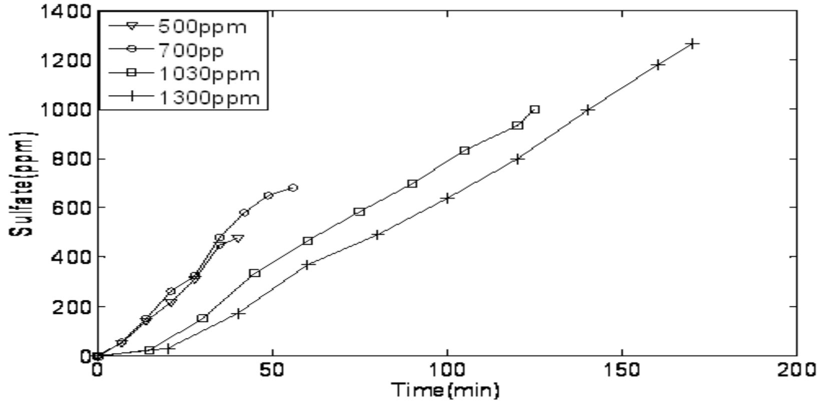


Figure-7: Relationship between time and sulfate formed during photo oxidation of sulfide

Under a particular set of experimental conditions, the bubbling air supplies oxygen at a sufficiently high rate so that its concentration remains practically constant. The oxygen consumed by the sulfide ions is immediately replenished by absorption from the air bubbles. As sulfide becomes converted to sulfate, the pH drops and tends to move towards the neutral value of 7. It was found that higher the atmospheric airflow rates to the opening of the sparger, the faster the sulfide oxidation of the liquid. This is because the higher the atmospheric airflow rates to the opening of the sparger, the larger the concentration of oxygen in the liquid. The larger concentration of oxygen in the liquid will allow more reaction with the excited sulfide ions in the liquid. Increased reaction will shorten the time to oxidize the sulfides in the liquid. Rate of formation of sulfate is higher at high air flow rates. Final concentration of sulfate at the end of oxidation process of sulfate is nearly equal to the initial concentration of sulfide. Formation of sulfate during oxidation of sulfide at different air flow rates has been shown in the Figure-10. It was found that higher the oxygen partial pressure in the gas supplied to the opening of the sparger, the faster the sulfide oxidation of the liquid. This is because the higher is the oxygen partial pressure in the gas supplied to the opening of the sparger, the larger is the concentration of dissolved oxygen in the liquid. The larger concentrations of oxygen in the liquid will allow more reaction with the excited sulfide ions in the liquid. Increased reaction will shorten the time to oxidize the sulfides in the liquid. Rate of sulfide oxidation was found to be faster at high oxygen partial pressure in the gas. Effect of different oxygen partial pressures on photo oxidation of sulfide has been shown in Figure-11.

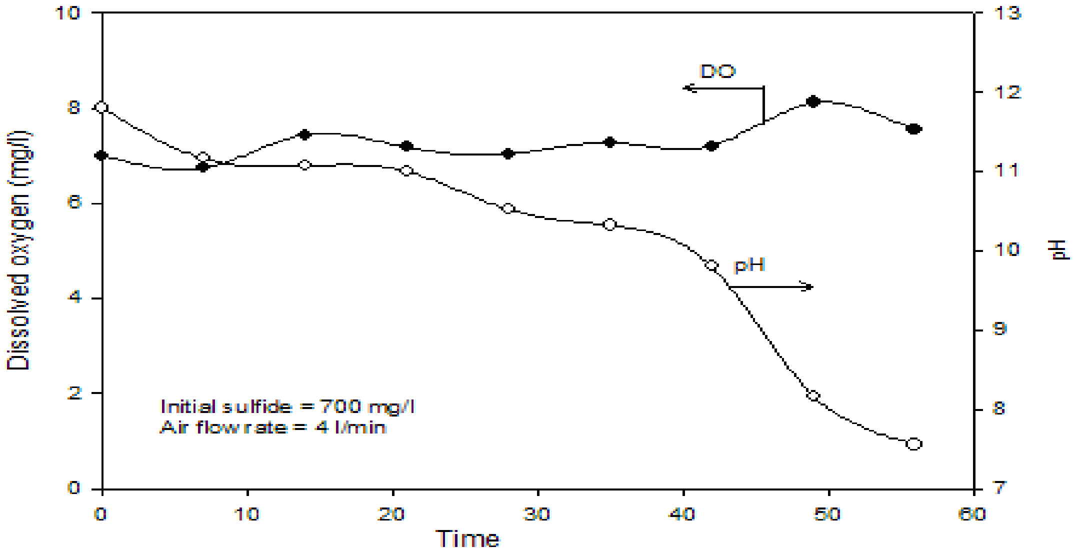


Figure-8: Relationship between time, pH and dissolved oxygen during the photo aeration

Rate of formation of sulfates was found to be higher at high oxygen partial pressures. It was found that the sulfate formed was approximately equal to the initial concentration of sulfide during the oxidation of sulfide at different oxygen partial pressures. Sulfate formation at different oxygen partial pressures has been shown in the Figure-12. It was found that stronger the UV irradiation from the UV light, the faster the sulfide oxidation in the liquid. This is because with the increase in the UV irradiation intensity from the UV light, the amount of excited sulfide ions in the liquid is increased. The larger amount of excited sulfide ions in the liquid will allow more interaction with the oxygen in the liquid. Increased reaction will shorten the time to oxidize the sulfides in the liquid. Rate of sulfide oxidation was found to be faster at high intensity of UV light.

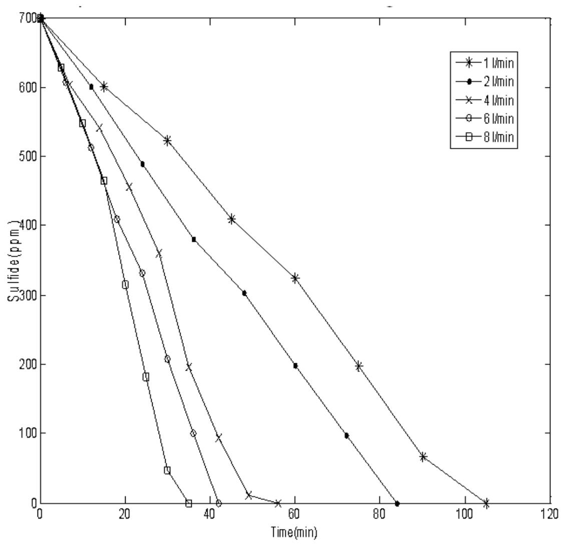


Figure-9: Relationship between time and concentration during oxidation at different air flow rates

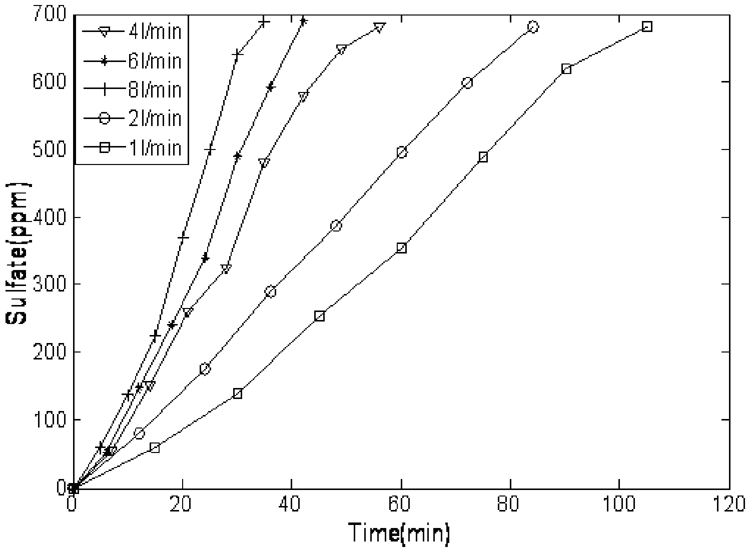


Figure-10: Relationship between time and sulfate formed during oxidation at different air flow rates.

The rate of formation of sulfate is also faster at high intensity of UV light. The concentration of sulfate formed during the oxidation of sulfide is almost same at different UV light intensities.

The effect of different UV light intensity on sulfide oxidation has been shown in Figure-13. It was observed that the concentration of sulfate formed was 682 ppm for the oxidation of 700 ppm of sulfide with 4 watts UV light intensity. For the complete oxidation of similar amount of sulfide with 8 watts UV light intensity the concentration of sulfate was found to be 689ppm. But the time of oxidation was found to be 35 minute in the case of 8watts intensity as compared to 56 minutes with 4 watts of UV light intensity. The sulfate formation has been shown in the Figure-14. Oxidation of industrial wastewater was done in order to prove that the process is effective for the industrial sample of wastewater which is the primary purpose. Oxidation of sulfide in an industrial wastewater sample, having the airflow rate of 4 liter/min and UV irradiation of 12W intensity has been shown in Figure-15.

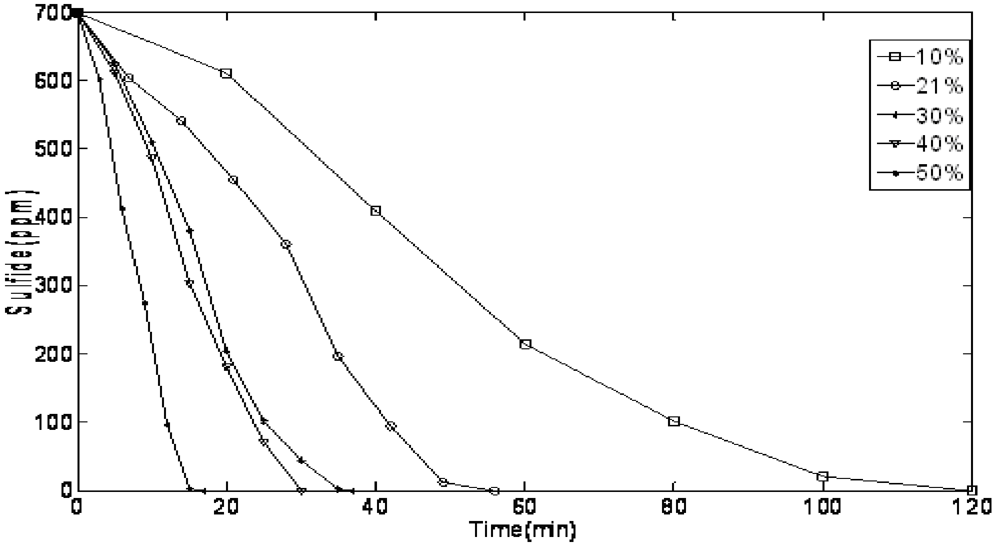


Figure-11: Relationship between time and sulfide at different oxygen partial pressures.

It was found that the concentration of sulfides decreased during the oxidation. It can be related to reaction between photo-excited sulfide ion and dissolved oxygen. The initial concentration of sulfide in industrial wastewater is 4800mg/liter. It was found that oxidation of sulfide in the industrial wastewater took more than six hours. The required time for oxidation was more than the expected time. This can be related to the presence of thiosulfates, organics and in-organics in the industrial wastewater, as some part of the oxygen was consumed in the oxidation of thiosulfates, overcoming biological and chemical demands in the wastewater.

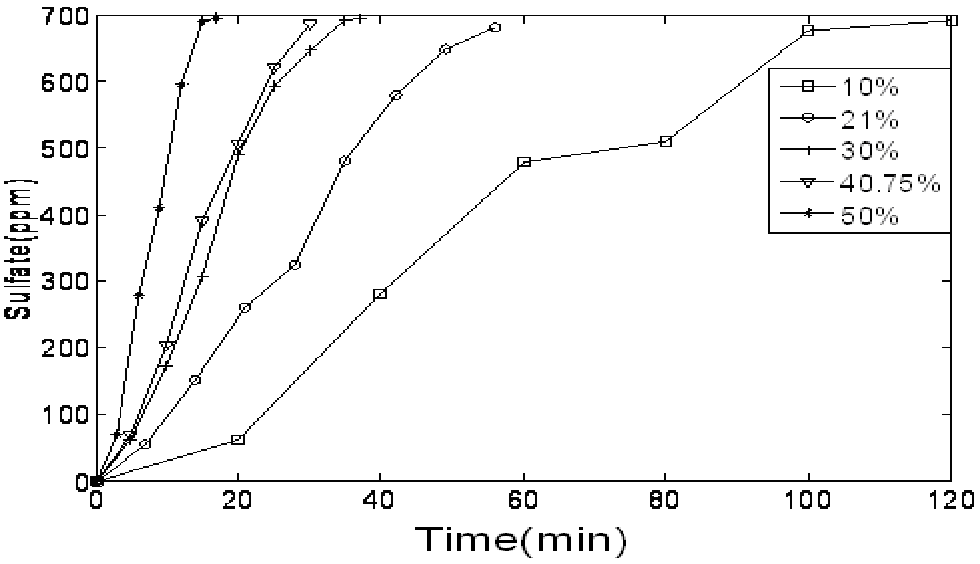


Figure-12: Relationship between time and sulfate formed at different oxygen partial pressures

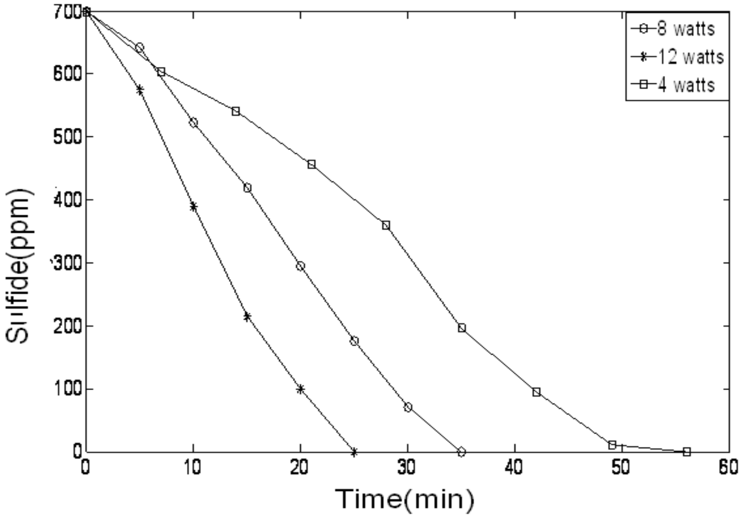


Figure-13: Relationship between time and sulfide during oxidation at different UV light intensities

4.1.1 Kinetics of photo aeration

5.1.2 Rate equation for sulfide oxidation

Rate of oxidation of sodium sulfide and hydrogen sulfide by dissolved oxygen has been represented by power-law kinetics [78].

$$r = K_1\,[\text{Oxygen}]^{m1}\,[\text{Sulfide}]^{m2} \qquad (12)$$

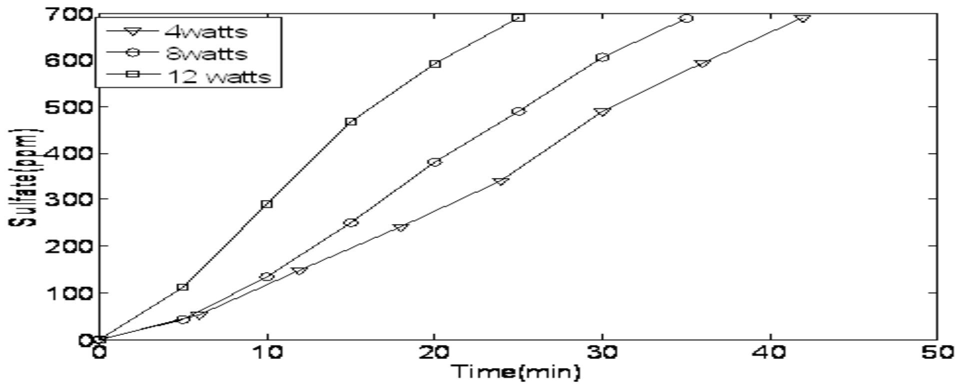


Figure-14: Relationship between time and sulfate formed at different UV light intensities

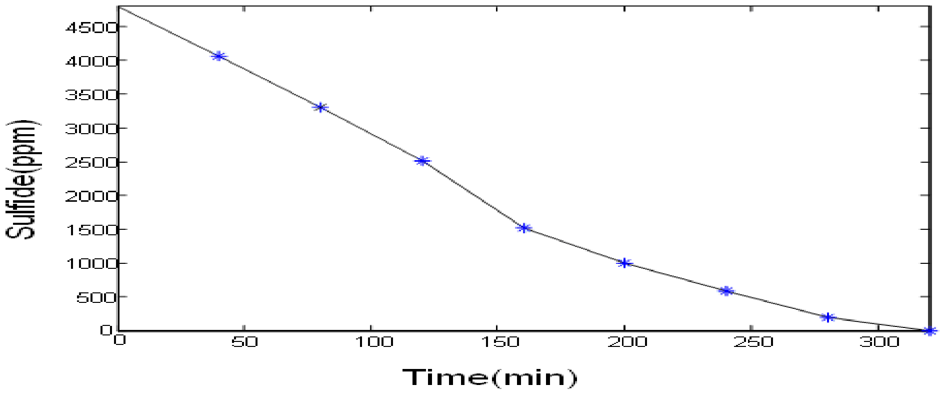


Figure-15: Relationship between time and sulfide of industrial sample during oxidation

Where K_1 is the rate constant and m_1 and m_2 are orders of reaction with respect to oxygen and sulfide respectively. A plot of the rate of sulfide oxidation against initial sulfide concentrations on a logarithmic scale at a constant air flow rate and UV light intensity gives the order $m_2 = 2$ as shown in Figure-16.

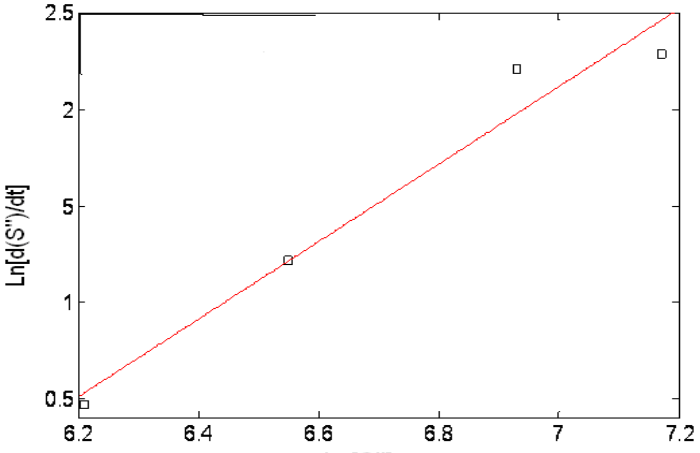


Figure-16: Linear plot of ln [d(S^{-2})/dt] against ln[S^{-2}]

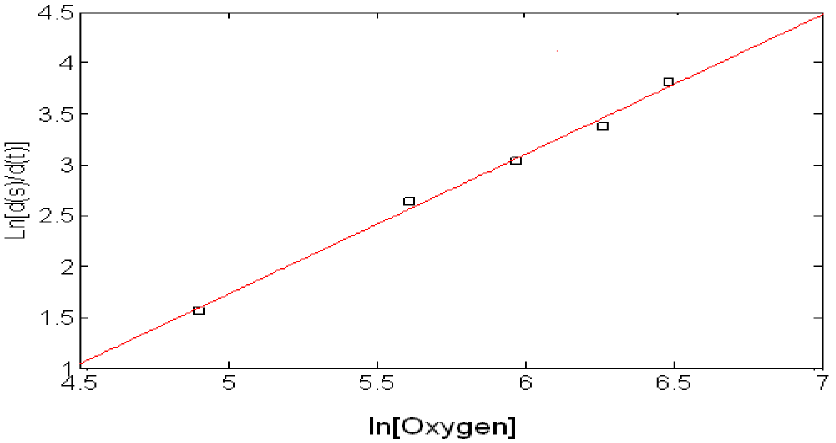


Figure-17: Linear plot of ln [d(S-2)/dt] against ln [Oxygen]

Therefore, it may be concluded that the reaction with respect to sulfide concentration follows second order kinetics. The reaction orders with respect to oxygen was similarly found out by plotting the initial rate of oxidation against the different partial pressures of oxygen on a logarithmic scale for constant values of all other parameters and variables as shown in Figure-17. The value of m_1 is 1.4 which is the order of reaction with respect to oxygen. The reaction rate constant, k, was determined from the slope of the plot of reaction rate against the product of two concentration terms in Eq. (1) as shown in Figure-18.

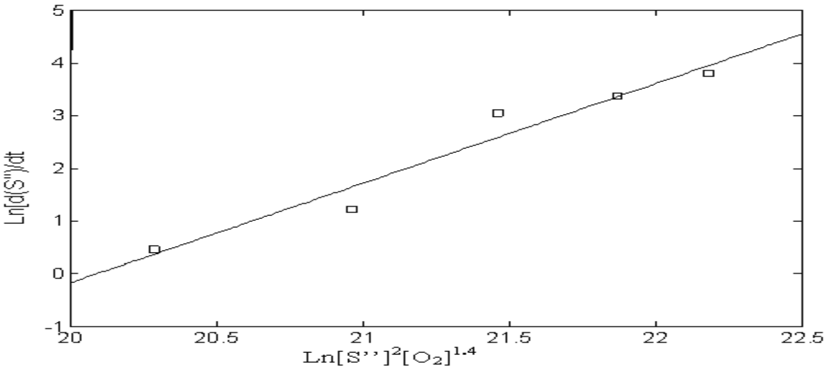


Figure-18: Linear plot of ln [d(S^{-2})/dt] against ln[S^{-2}]^2[O_2]$^{1.4}$

4.1.2 Rate equation for sulfate formation

Rate equation for sulfate formation is given below.

$$r = K_2\,[\text{Oxygen}]^{m_3}\,[\text{Sulfide}]^{m_4} \qquad (13)$$

Where K_2 is rate constant of sulfate formation while m_3 and m_4 are orders of reaction with respect to oxygen and sulfide respectively. Order of reaction with respect to oxygen in the sulfate formation was found to be 1.2. It was found by plotting the rate of sulfide oxidation against the different initial oxygen partial pressures on logarithmic scale as shown in the Figure-20.

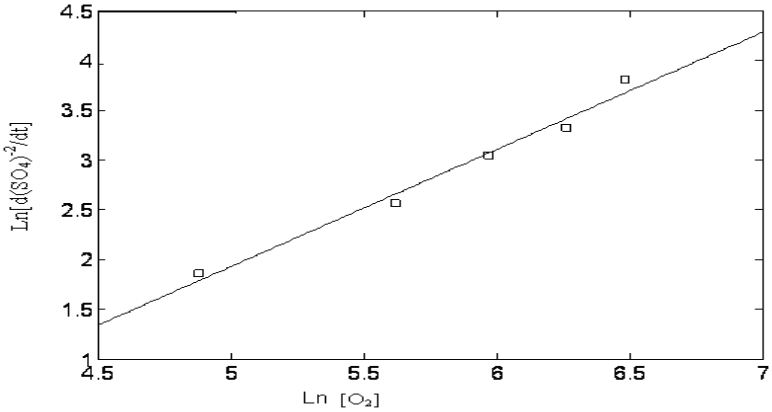


Figure-19: Linear plot of ln [d(S-^{2})/dt] against ln [O2].

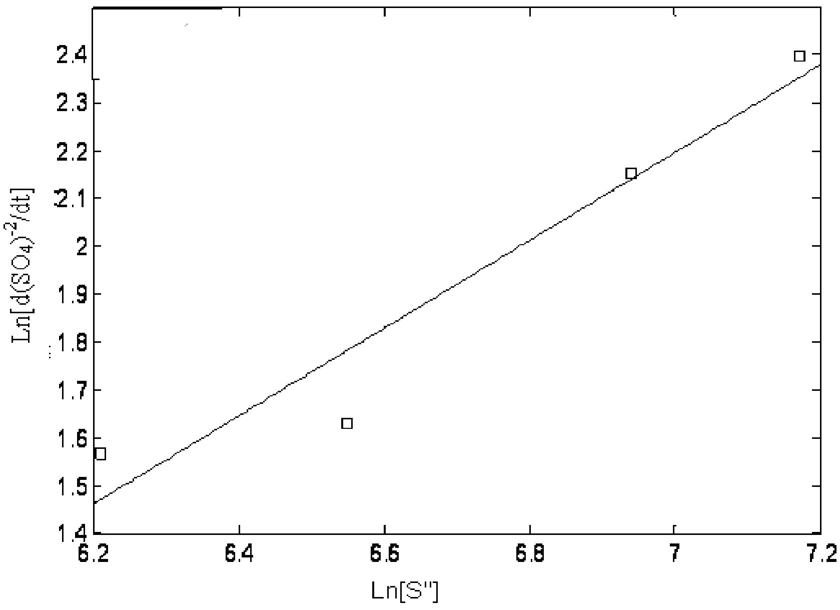


Figure-20: Linear plot of ln [$(SO_4)^{-2}$/dt] against ln[S'']

Similarly the order of reaction with respect to sulfide concentration was found by plotting sulfide oxidation rate against the different initial sulfide concentrations. The order with respect to sulfide was found 0.92 as shown in Fig19. Rate constant for sulfate formation was found by plotting sulfide oxidation rate against the product of oxygen and sulfide concentrations as shown in Figure-21.

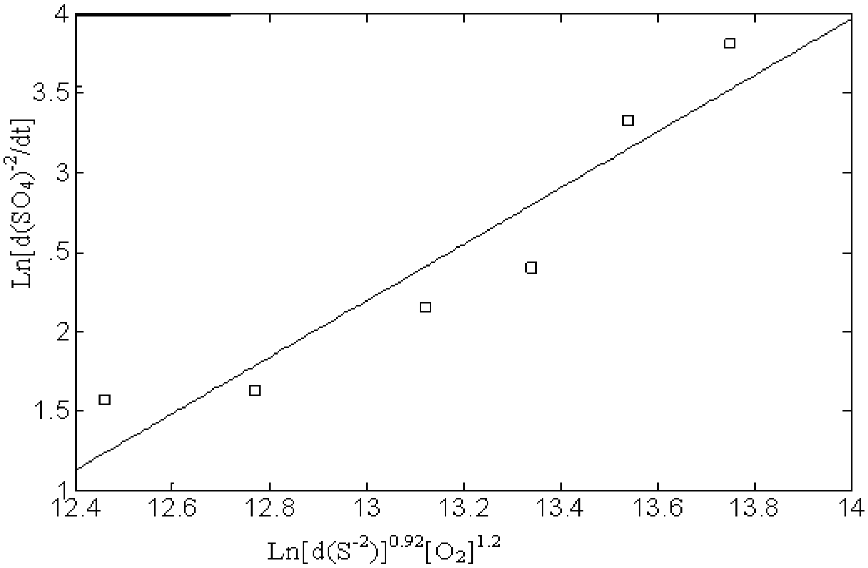


Figure-21: Linear plot of ln [$(SO_4)^{-2}$/dt] against ln[S’’]$^{0.92}$[O2]$^{1.2}$

4.2 Catalytic Oxidation of Sulfide by hydrogen peroxide

Oxidation of sodium sulfide was carried out by oxidation in the presence of ferric oxide catalyst. The process has been investigated by using different hydrogen peroxide addition, different catalyst loading, different initial sodium sulfide concentrations and different temperatures. The experiment was done at different initial concentrations of sulfides, different catalyst loading, different hydrogen peroxide addition and at different temperatures. Experimental data of the catalytic oxidation by hydrogen peroxide has been shown in the appendix (table-15 to table-27).

4.2.1 Characterization of catalyst

The catalyst used in this process was synthesized in the laboratory as described in the experimental part. Characterization of the catalyst was done by SEM, EDX and FT-IR. In the FT-IR spectra of the catalyst sample (Figure-22) no stretching frequency of either free water (above 3600cm^{-1}) as well as bonded water (above 3400 cm^{-1}) was observed. The spectral band at 3139cm^{-1} was due to stretching vibration of traces of inner lying OH^{-} ions in the sample. Bending vibrations of the OH groups was observed at 1632cm^{-1} and 1402cm^{-1} respectively. The band at 1402cm^{-1} was assigned to out of plane bending vibration whereas the band at 1632cm^{-1} was due to the in-plane bending vibration. The band at 576cm^{-1} was assigned to Fe-O stretching vibration. The material contains traces of isolated Fe-OH bonds and no free water. The cationic field of Fe was significant in the sample, possibly due to the presence of more polarizing Fe^{3+} as the bending vibration of OH^- was split in two planes. Thus the material can be called hydrated ferric oxide or synthetic ferric oxide with ‘defect’.

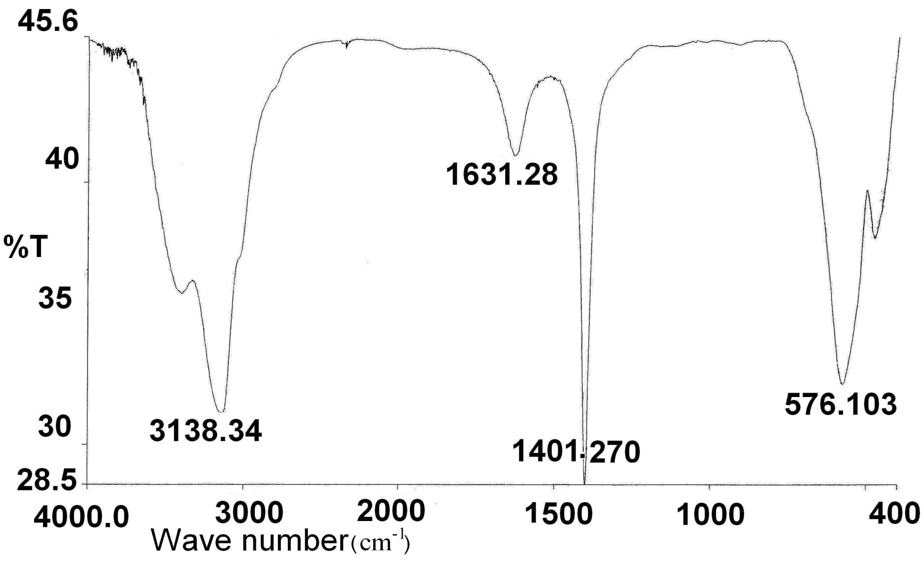


Figure -22: FT-IR Spectrum of Ferric Oxide

The peak at 35.7^0 is the most intense peak of Fe_2O_3 in XRD spectrum [81]. The XRD picture (Figure-23) shows synthetic ferric oxide (Hematite) as the major crystalline phase. The relative intensity of the phases indicated incomplete crystallization.

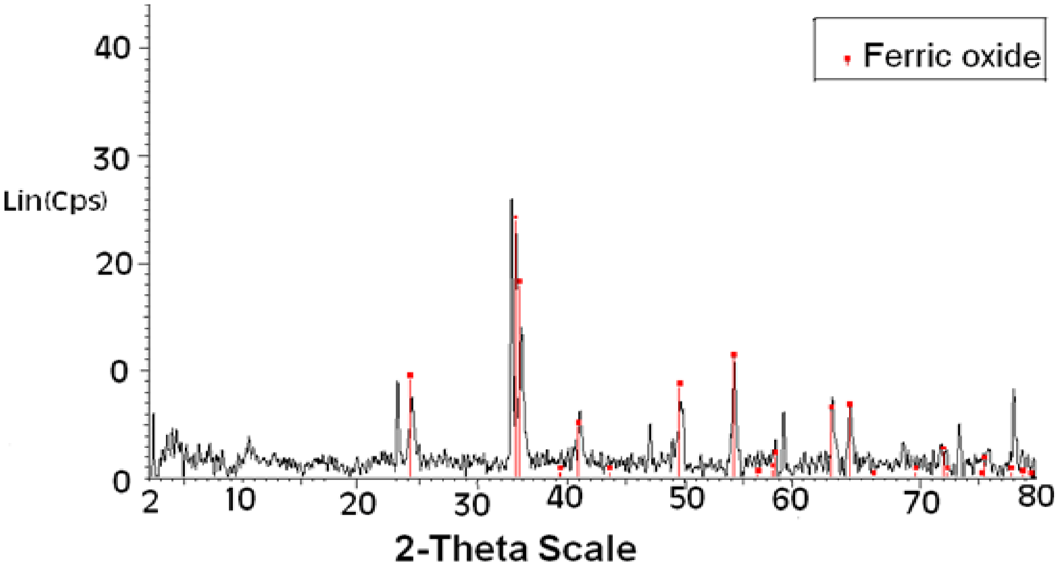


Figure-23: XRD spectrum of Ferric Oxide catalyst

In the SEM photograph of the sample (Figure-24), spherical isolated particles of submicron size was observed. The particle size distribution was narrow and some local weak agglomerate formation was observed. Average particle size was less than 200nm. Elemental analysis was confirmed from the EDX study that the sample basically contained Fe, O and H as the major elements. Trace amount of Cl was also observed in the sample. It comes from ferric chloride which is the starting material for catalyst preparation.

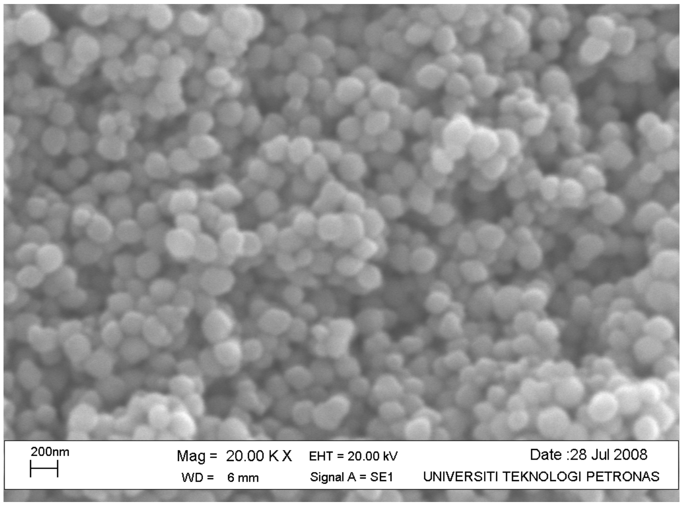


Figure-24: SEM picture of the ferric oxide catalyst at 20X

Oxidation of sulfide in an aqueous solution proceeds through the following reaction pathway [83]:

$$\begin{tikzcd} & S & & & \\ S'' \arrow[ur] \arrow[r] & S_2O_3'' \arrow[r] & SO_3'' \arrow[r] & SO_4'' & (3) \end{tikzcd}$$

The rate as well as the final oxidation product depends upon the availability of oxygen and the pH. The rate of sulfite oxidation to sulfate is very fast in an oxidizing environment. Therefore the formation of an intermediate $SO3^{2-}$ may be ignored and the scheme may be simplified as:

$$S'' \longrightarrow S_2O_3'' \longrightarrow SO_3'' \longrightarrow SO_4'' \qquad (4)$$

Oxidation of sulfide by Fenton's reagent has been studied by Ksibi et al [26]. He found that during the Fenton reaction ferrous ion converts to ferric ion. Ferric ion oxidize sulfide to elemental sulfur and reduce itself to ferrous ion which removes sulfide by converting it to ferrous sulfide.

In the present work the important parameters that determine the rate of sulfide oxidation are: (i) the sulfide concentration, (ii) H_2O_2 concentration, and (iii) catalyst loading. Adjustment of the pH to nearly neutral could be done with the addition of acid but it generates H_2S in solution. To avoid the formation of H_2S that might escape from the solution to some extent, we conducted all the experiments at the prevailing pH of the solution. However, change of the pH occurred in course of the oxidation process. As the oxidation proceeds, sulfide concentration decreased and the pH also decreases.

Figure-25 shows the time evolution of sulfide concentration for four different initial values. All these data were collected with synthetic wastewater samples. The same amount of hydrogen peroxide 2.6 ml, 30% solution, w/w) was added to each batch of 500 ml sulfide solution. The initial rate of sulfide oxidation showed an appreciable dependence on the initial concentration. The rate appears higher at a lower initial concentration contrary to what is expected. Beginning with 1000 ppm sulfide solution, complete removal of the sulfide could be achieved within about 55 minutes.

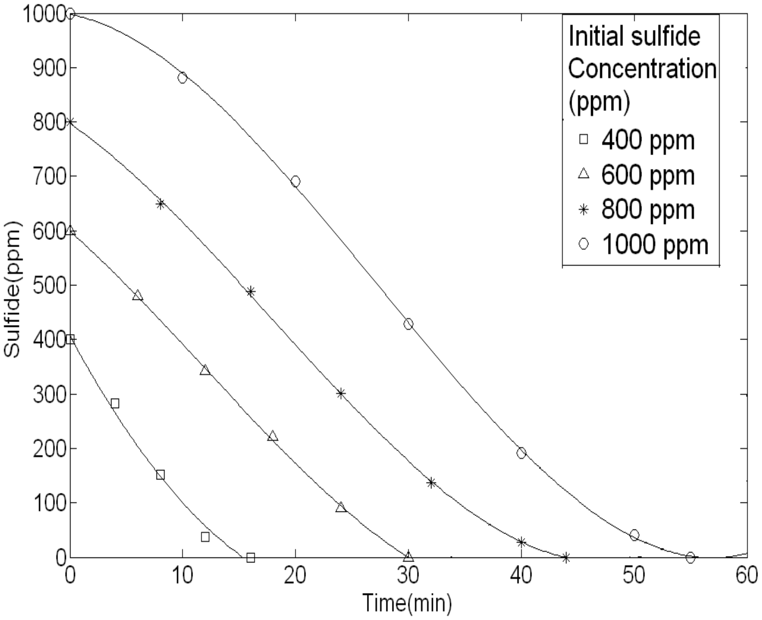


Figure-25: Relationship between time and sulfide during oxidation at different intial sulfide concentrations

The effect of catalyst loading which was varied from 0.25 to 1.5 gm in 500 ml feed solution has been investigated. The time of complete sulfide removal varies from 17 to 90 minutes. The pH of the solution decreased gradually from an initial value of 11.2. It was found that the rate of oxidation increased with the increasing in the catalyst loading. Oxidation of sulfide at constant hydrogen peroxide addition and at different catalyst loading has been shown in Figure-26.

The effect of temperature on sulfide oxidation has been investigated. The rate of oxidation increases rapidly with the increase in temperature and the total time of sulfide oxidation changes from 30 minutes to about 6 min as the temperature increases from 298 to 318K.The effect of temperature on oxidation rate has been shown in Figure-27.

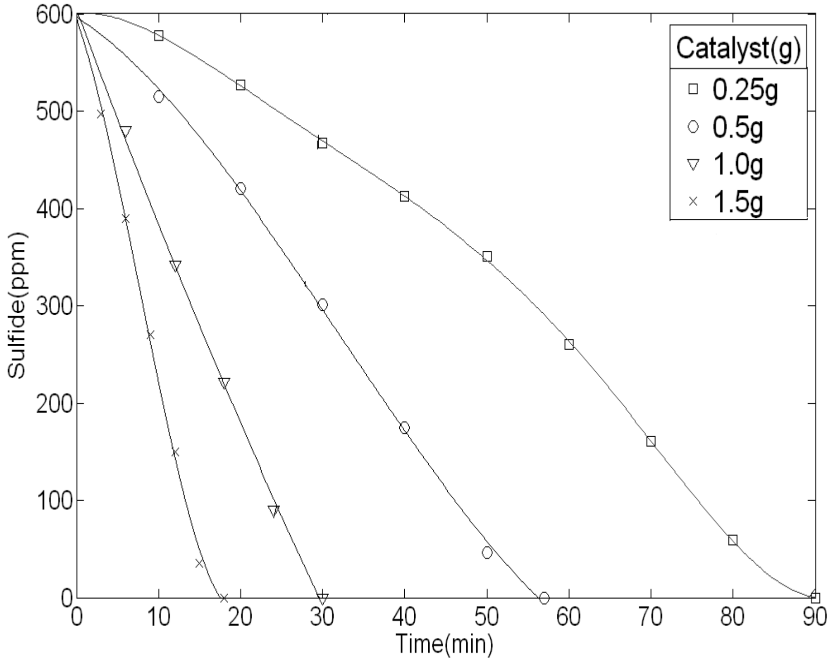


Figure-26: Relationship between time and sulfide during oxidation process at different catalyst loading

The effect of hydrogen peroxide addition on sulfide oxidation has been in investigated also. The rate of sulfide oxidation increased with the increase in the amount of hydrogen peroxide addition. With increase in the hydrogen peroxide amount from 1.8 to 3.2ml the rate of sulfide oxidation increases approximately five times. In all the cases of hydrogen peroxide addition,the concentration of sodium sulfide has been kept constant (600 ppm) with 1g of catalyst loading. We have also measured sulfate concentration in solution from time to time. Since the oxidation of sulfite to sulfate in the presence of H_2O_2 is fast, the solution virtually contains sulfide, thiosulfate and sulfate. The concentration of thiosulfate may be calculated from the measured concentration of sulfide and sulfate. The effect of hydrogen peroxide addition on oxidation process has been shown in Figure-28.

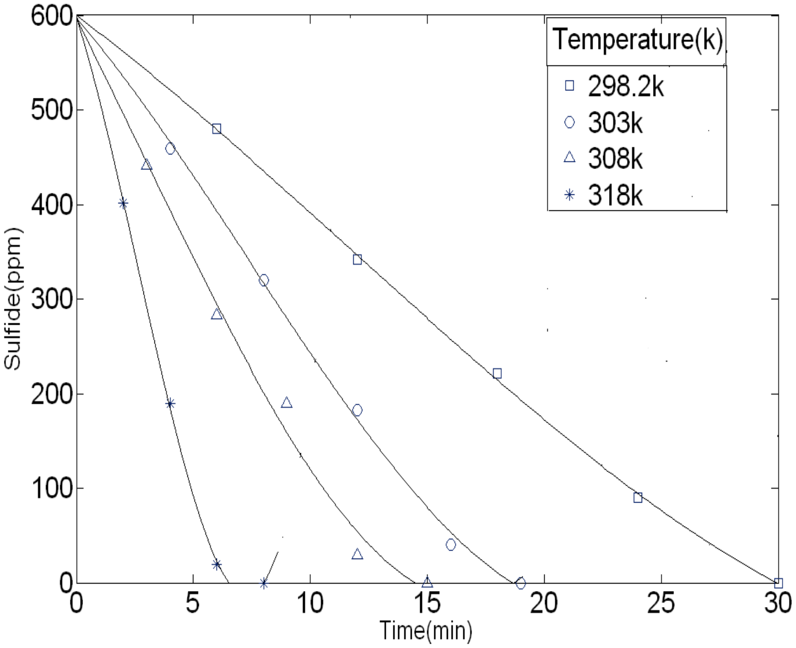


Figure-27: Relationship between time and sulfide during oxidation process at different temperatures

Figure-29 shows sulfate formation at different initial sulfide concentrations. Initial rate of sulfate formation was higher at high sulfide concentration. Later on the rate of formation of sulfate was higher at lower sulfide concentration. Catalyst loading and hydrogen peroxide addition were maintained during the oxidation of all initial sulfide concentrations.

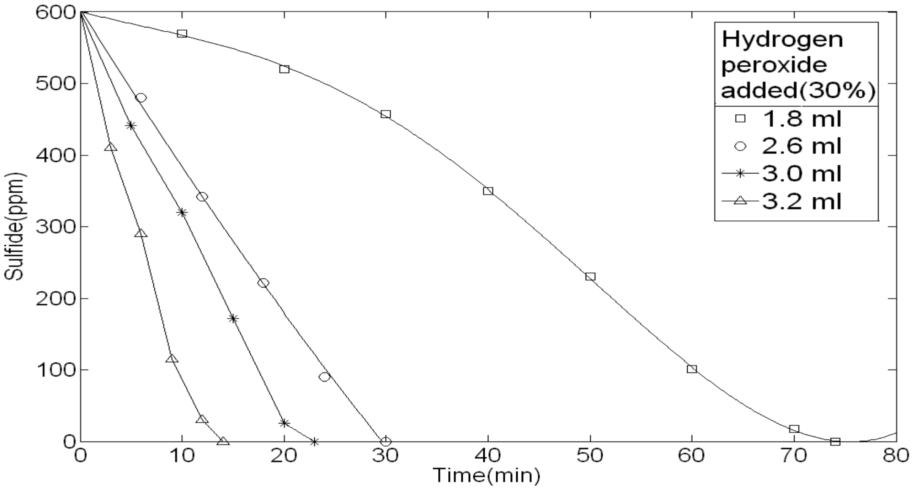


Figure-28: Relationship between time and sulfide at different hydrogen peroxide addition

Figure-30 shows sulfate formation at different catalyst loading, same hydrogen peroxide addition and same initial sulfide concentration. Rate of formation of sulfate increased with increasing catalyst loading. The sulfate formed was almost the same nearly equal to the initial sulfide concentration.

Figure-31 shows sulfate formation at different temperatures with the same amount of hydrogen peroxide addition, same catalyst loading and same initial sulfide concentration. Rate of sulfate formation increased with the increase in temperature. Higher temperature reduced the time required for oxidation of sulfide to sulfate.

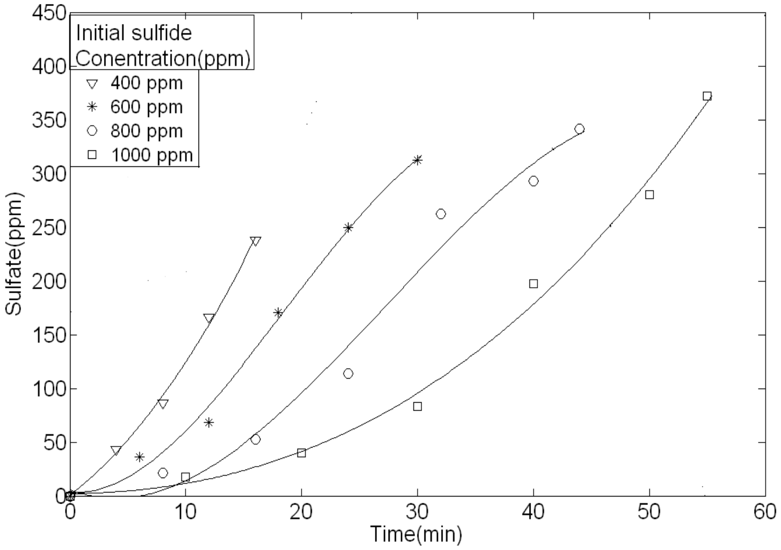


Figure-29: Relationship between time and sulfate formed at different initial sulfide concentrations

4.2.2. Kinetics of catalytic oxidation

4.2.2.1 Rate equation for sulfide oxidation

Rate of oxidation of sodium sulfide and hydrogen sulfide by dissolved oxygen has been represented by power-law kinetics [78]. For catalytic oxidation with H_2O_2; we propose the following rate equation.

$$r = K_3\,[\text{Sulfide}]^{x1}\,[H_2O_2]^{x2}\,[\text{Cat}]^{x3} \qquad (14)$$

Where the quantities within brackets represent the concentrations of sulfide, hydrogen peroxide and of the catalyst respectively. In this redox system where the oxidant (H_2O_2) and the reductant (S^{-2}) were present together in solution, it was not possible to estimate the concentration of hydrogen sulfide separately from time to time. We therefore, determined the kinetic constants from the initial rate and initial reactant concentrations, hydrogen peroxide and the catalyst loading. A plot of the initial rate against sulfide concentration on a logarithmic scale at a constant concentration of H_2O_2 and catalyst loading showed with 0.88 value, indicating a fractional order for the sulfide concentration.

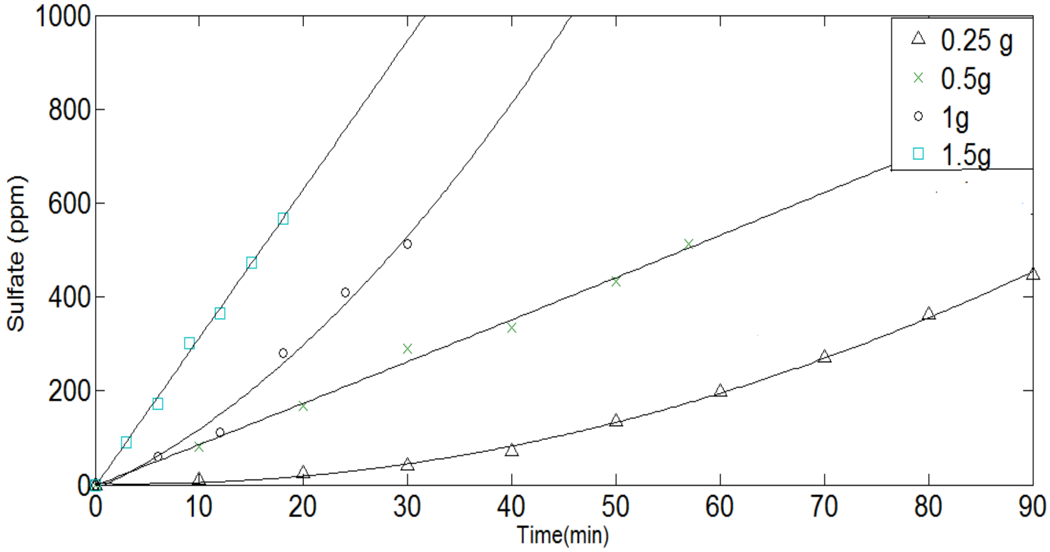


Figure-30: Relationship between time and sulfate formed at different catalyst loading

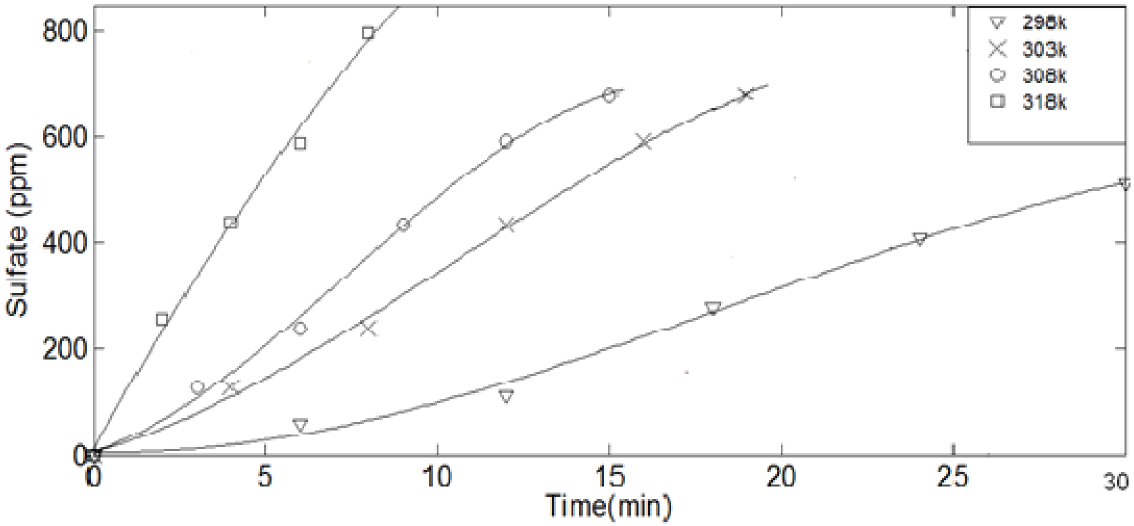


Figure-31: Relationship between time and sulphide at different temperatures.

The reaction orders with respect to H_2O_2 and the catalyst were similarly found out by plotting the initial rate against the respective concentrations on a logarithmic scale for constant values of all other parameters and variables. The plots of the initial rate of reaction against catalyst loading and against the H_2O_2 concentration were linear. Thus the reaction is first order with respect to both H_2O_2 and catalyst concentrations ($x_2 = 1$; $x_3 = 1$).

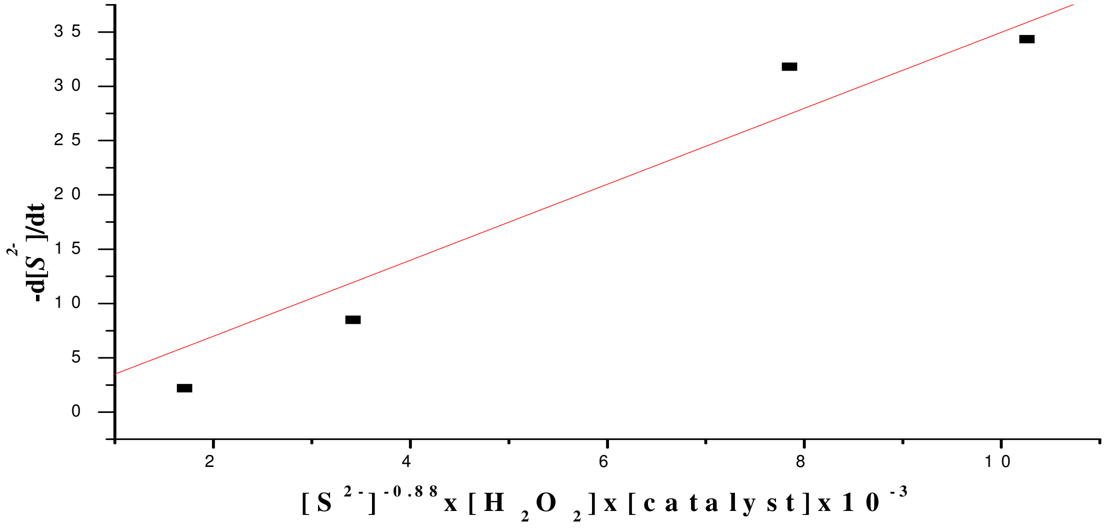


Figure-32: Linear plot between product of sulfide, catalyst and hydrogen peroxide and rate of sulfide oxidation

The reaction rate constant, *k*, was determined from the slope of the plot (Figure 32) of the initial reaction rate against the product of three concentration terms in Eq. (14).The exercise was carried out for the data collected at the four different temperatures. Figure.33 shows the Arrhenius plot of the rate constants. The activation energy determined from the slope of the line is E = 25.85 kcal/mol.

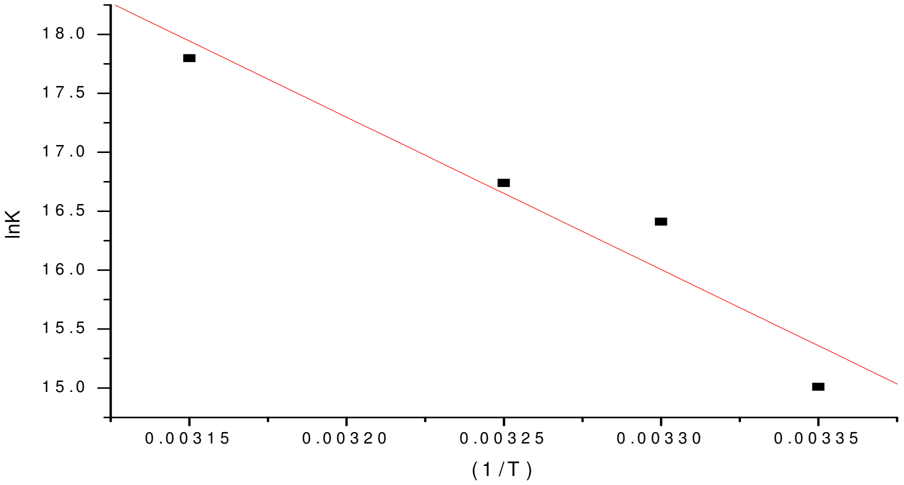


Figure- 33: Arrhenius plot of reaction rate for sulfide oxidation.

4.2.2. Rate equation for sulfate formation

Power law rate equation for the sulfate formation is given below, where the quantities within brackets represent the concentrations of sulfide, hydrogen peroxide and of the catalyst respectively.

$$r = K\,[\text{Sulfide}]^{y1}\,[H_2O_2]^{y2}\,[\text{Cat}]^{y3} \qquad (15)$$

A plot of the initial rate against sulfide concentration on a logarithmic scale at a constant concentration of H_2O_2 and catalyst loading showed $y_1 = 2.4$.

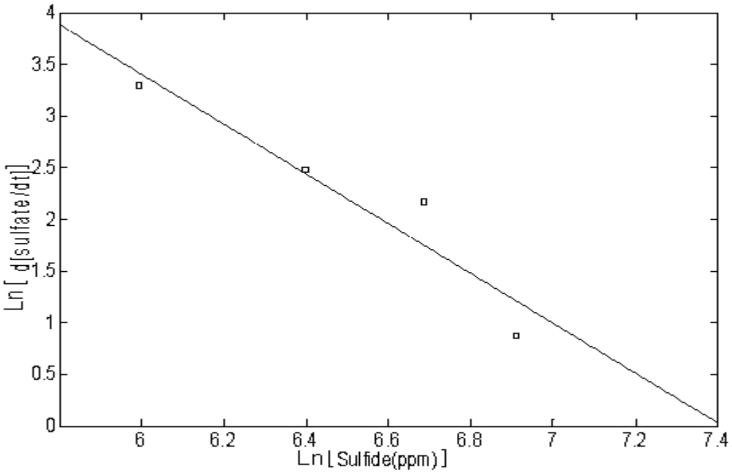


Figure-34: Linear plot between sulfide and rate of sulfide oxidation on logarithmic scale.

The reaction orders with respect to H_2O_2 and the catalyst were similarly found out by plotting the initial rate against the respective concentrations on a logarithmic scale for constant values of all other parameters and variables.

Plots of the initial rates of reaction against catalyst loading and against the H_2O_2 concentration were linear. Thus the reaction was near to first order with respect to both H_2O_2 and catalyst concentrations ($^{y2} = 1.1$; $^{y3} = 1.5$). The reaction rate constant, $k = 1.5$ was determined from the slope of the plot (Figure 35) of the initial reaction rate against the product of three concentration terms in Eq. (15).

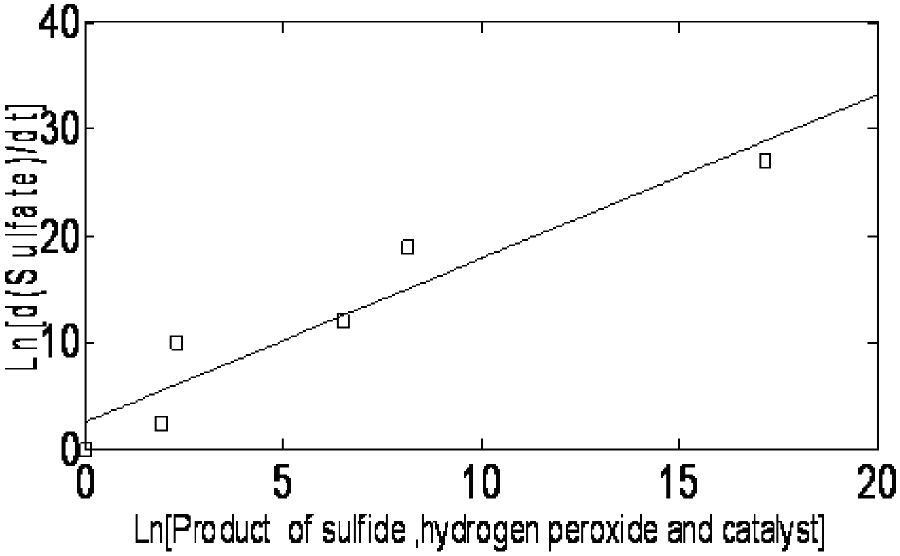


Figure-35: linear Plot for the determination of rate constant of sulfate formation.

4.3. Precipitation of Sulfides by Iron Salts

In precipitation process sodium sulfide was removed by treating sulfidic wastewater with different Fe^{+2}/Fe^{+3} ratio bearing iron salts. The residual sulfide in the wastewater was removed by aeration. The effect of sulfide concentration, Iron salts, temperature on sulfide removal by precipitation and residual sulfide removal by aeration using different air flow rate has been given in the appendix (table-28 to table-41).

Precipitation of sulfide in an aqueous solution proceeds through the following reaction pathway [14]:

$$Fe^{2+} + HS^{-} \rightarrow FeS + H^{+} \qquad (16)$$

$$2Fe^{3+} + HS^{-} \rightarrow 2Fe^{2+} + S^{0} + H^{+} \qquad (17)$$

Fe^{+2} can remove sulfides by precipitation as ferrous sulfides (FeS) according to Eq (16). Fe^{+3} can remove sulfides by oxidizing it chemically to elemental sulfur while being reduced to Fe^{+2} which can subsequently produce FeS [(Eq.(16) and Eq(17)].

Precipitation of sulfides was faster in the beginning but became slow later. It can be related to high solubility of sulfide in wastewater and very low solubility of iron salts, in the wastewater.

We have used different iron salts ratios for the sulfide precipitation as shown in Figure 36. Precipitation of 500 ppm of sulfide took 55 min by using Fe^{+2}/Fe^{+3} ratio of 0.3. It was observed that the rate of sulfide precipitation became faster at higher ratio Fe^{+2}/Fe^{+3}.

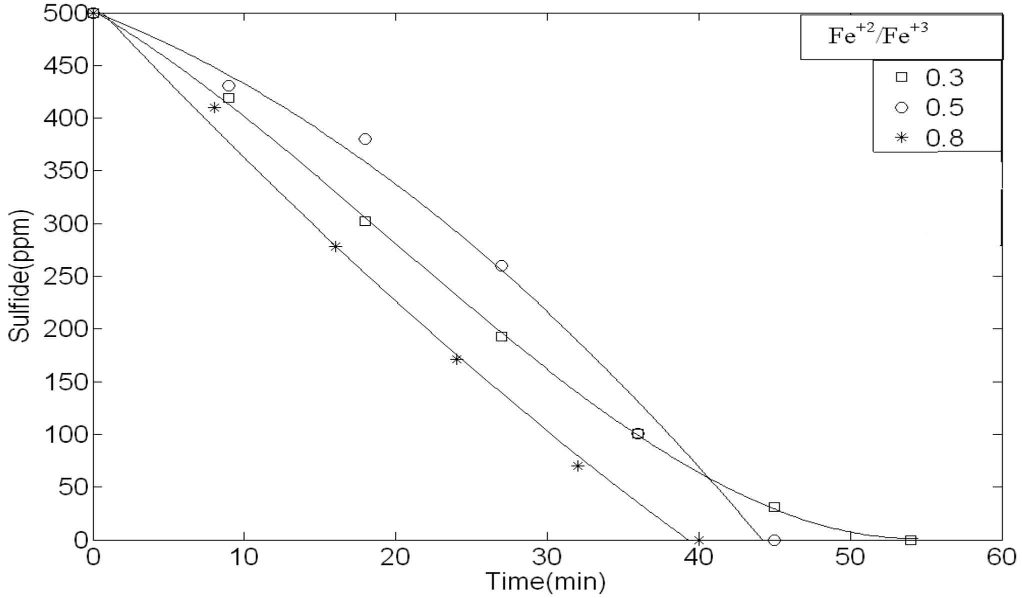


Figure-36: Time-concentration plots of sulfide removal.

Precipitation of 500 ppm sulfide took 40 minutes by using Fe^{+2}/Fe^{+3}ratio of 0.8. All these data were collected by treating synthetic wastewater samples. Initial pH of the sulfide solution was between 11 and 12 depending upon the initial concentration of sulfide solution. At the end of treatment pH was found between 3 and 4 for industrial sample and 5 to 6 for synthetic sample.

Figure-37 showed the time evolution of sulfide concentration for three different initial values of sulfide concentration. Fe^{+2}/Fe^{+3} ratio of 0.5 ratio was added to each batch of 1000ml sulfide solution. The rate of sulfide precipitation was higher at high sulfide concentration. Beginning with 1000 ppm sulfide solution, complete removal of sulfide was achieved within about 100 minutes.

The sulfide precipitation was investigated by using Fe^{+2}/Fe^{+3} ratio of 0.5 ratio at different temperatures. Figure -38 shows the effect of temperature on sulfide precipitation. The rate of sulfide precipitation increased with temperature and the total time of sulfide precipitation changed from 45 min to about 30 minutes as the temperature was increased from 298 to 338K.

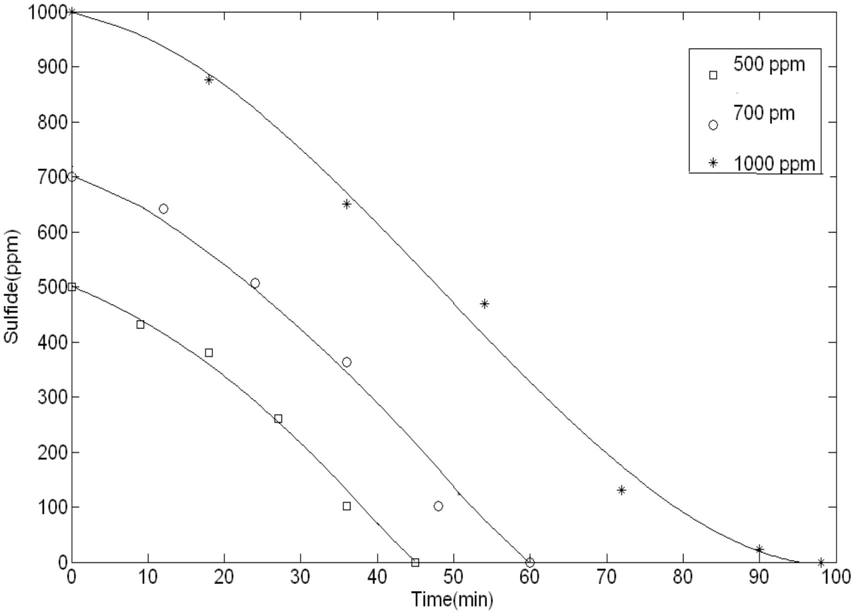


Figure-37: Time -concentration reduction plots of sulfide by iron salts at different initial sulfide concentrations

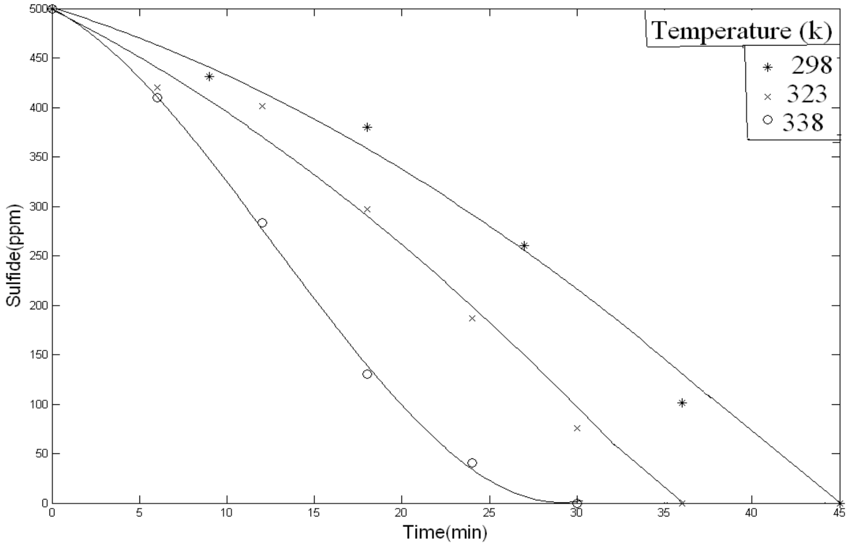


Figure-38: Time-concentration plots of sulfide reduction at different temperatures

4.3.1 Application to Industrial Wastewater

Industrial wastewater of methyl tertiary butyl ether preparation unit of PETRONAS Malaysia was treated by using iron salts followed by aeration. Wastewater contained higher concentration of sulfide. Analysis of sulfide of this industrial wastewater sample by methylene blue method showed 4800ppm which is significantly high concentration.

Industrial wastewater was treated by using different Fe^{+2}/Fe^{+3} ratios as shown in Figure-39. At higher iron salts ratio rate of precipitation was higher**.**

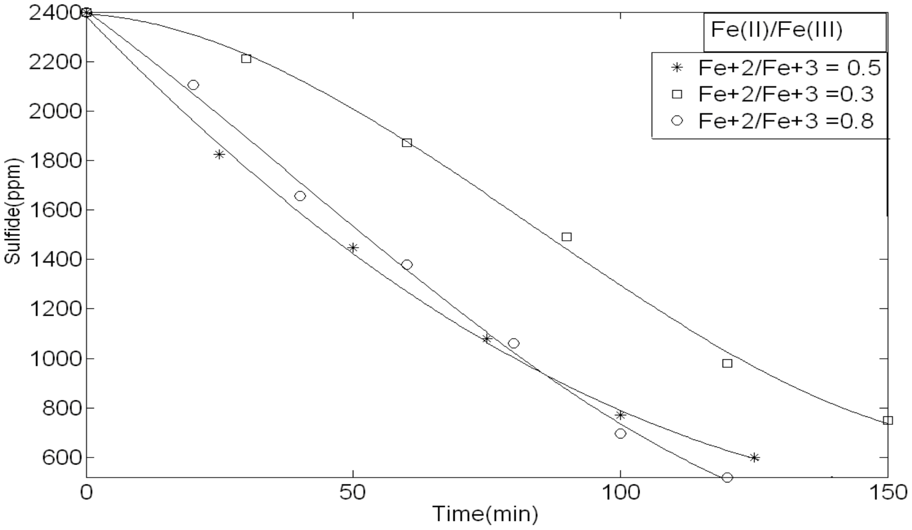


Figure-39: Time-concentration plots of sulfide removal from industrial wastewater at different Fe^{+2}/Fe^{+3} ratios

Figure-40 shows time evolution of sulfide concentration for industrial wastewater. Iron salts ratio of 0.5 was added to a batch of 1000ml sulfide solution. Total weight of both iron salts added was 17.1g which was stoichiometric amount of iron salts required. Initial concentration of sulfide in industrial wastewater was 4800 ppm. The concentration of sulfide after 220 minutes was found to be about around 1300 ppm. There was no further drop observed in the concentration of sulfide after this point. The drop in sulfide concentration was found negligible after this point. The residual sulfide after precipitation was removed by aeration. Figure-41 showed plots of sulfide removal by aeration at three different air flow rates. It was found that the rate of sulfide removal increased significantly at a higher air flow rate. It was concluded that complete removal of sulfide could be achieved by precipitation followed by aeration.

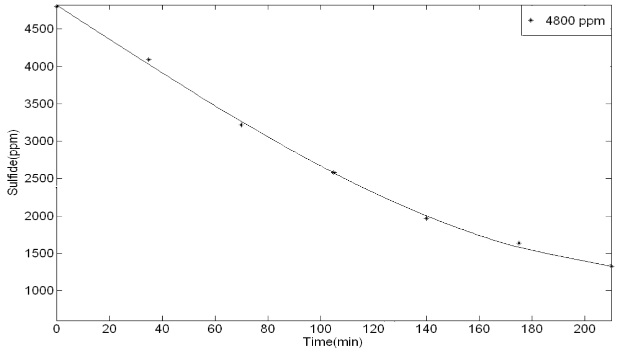


Figure-40: Time-concentration plots of sulfide removal for industrial wastewater

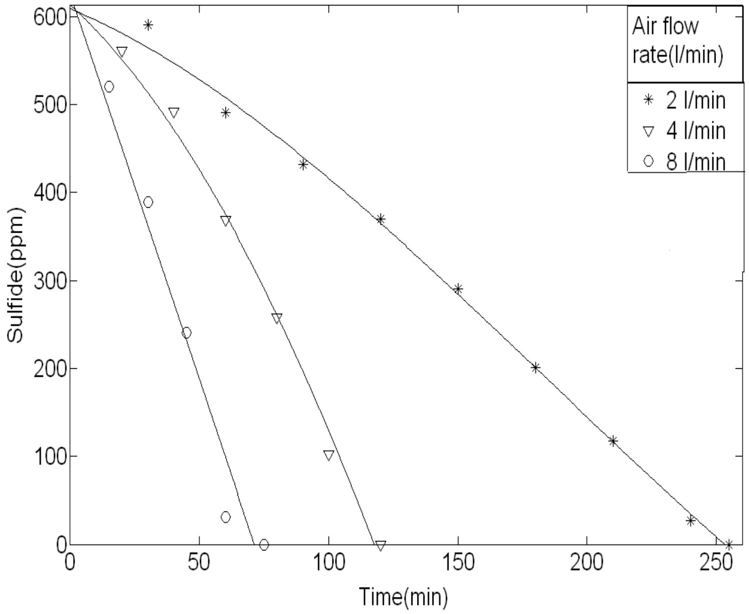


Figure -41: Relationship between time and sulfide at different air flow rates

4.3.2 Precipitation kinetics

We suggest the following rate equation for the precipitation.

$$r = K_4 [\text{Sulfide}]^{z1} \qquad (18)$$

Where z_1 is the order of reaction with respect to sulfide, K_4 is reaction rate constant .Precipitation kinetics was studied by measuring sulfide concentration against time for different ratios of Fe^{+2}/Fe^{+3}.The initial rates of sulfide removal were determined for each of these ratios and for different values of initial sulfide concentrations. Figure.42 shows plots of the reaction rate against sulfide concentration on a logarithmic scale at 0.5 ratio of iron salts.

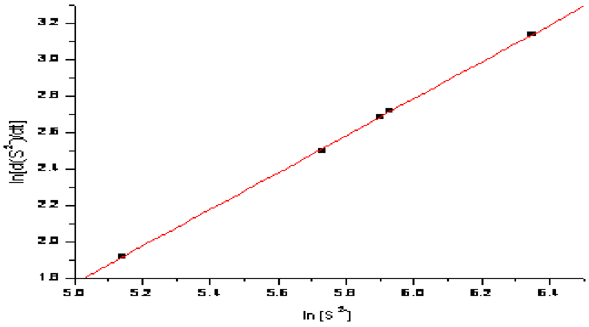


Figure-42: Linear fit of $\ln[d(S^{-2})/dt$ Vs $\ln[S^{-2}]$ at $Fe^{+2}/Fe^{+3} = 0.5$

The reaction rate calculated from the slope was unity. Thus the sulfide precipitation reaction was first order in sulfide concentration at 0.5 ratio of iron salts. Order of reaction for sulfide concentration was found to be unity at 0.3 and 0.8 both ratios as shown in Figures-43 and 44.The values of the rate constants were calculated at three different temperatures. The activation energy obtained from the Arrhenius plot was 22 kcal/mol as shown in Figure-45.

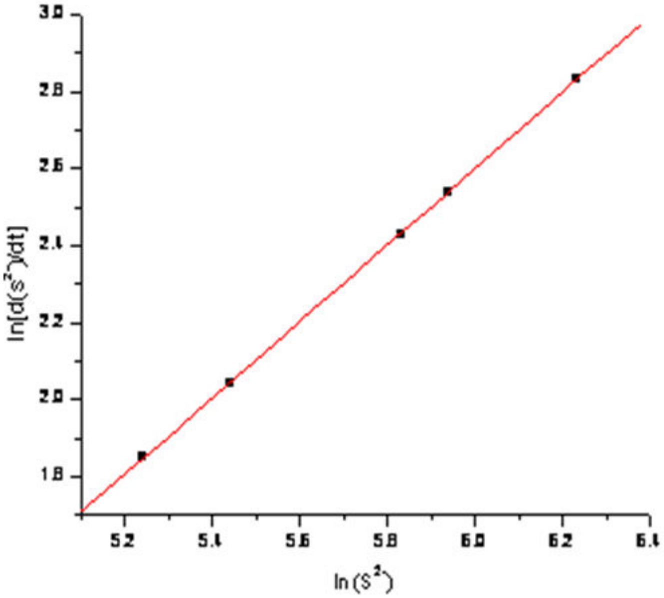


Figure -43: Linear fit of ln[d(S^{-2})/dt Vs ln[S^{-2}] at Fe^{+2}/Fe^{+3} =0.3

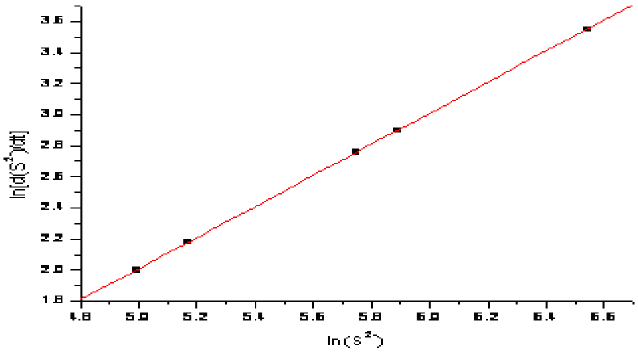


Figure- 44: Linear fit of ln[d(S^{-2})/dt Vs ln[S^{-2}] at Fe^{+2}/Fe^{+3} =0.8

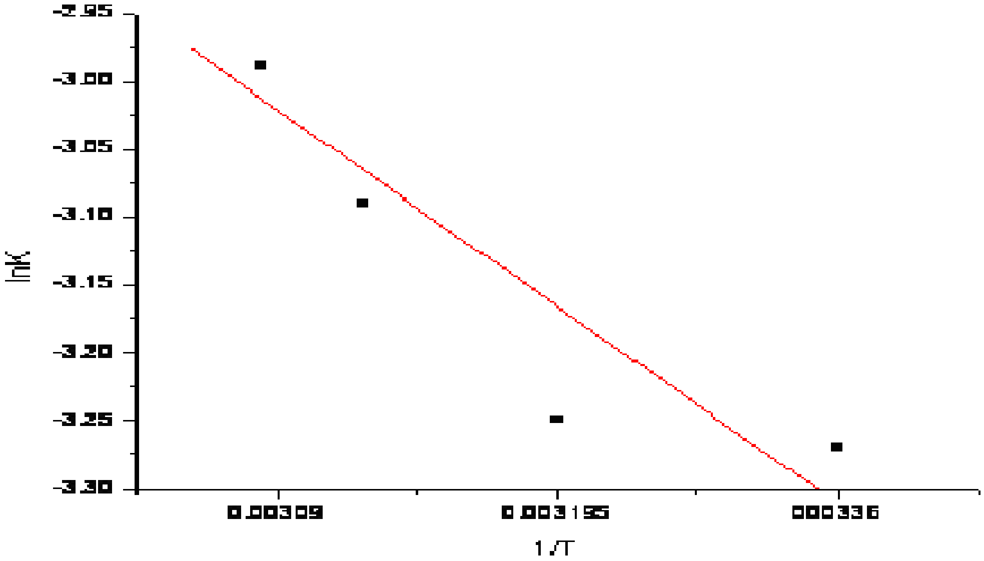


Figure-45: Arrhenius plot for precipitation of sulfide at Fe^{+2}/Fe^{+3} = 0.5

4.3.3 Characterization of the Precipitate

Figure- 46. Showed the SEM picture of a sample of the precipitated sulfide. No distinct or definite size of the particles was observed. The particles appeared in the form of irregular clusters with flaky shapes. The size distribution of the flakes was wide and the average size was estimated to be 500nm. From the EDX analysis (not shown here) it was confirmed that Fe and S were the major elements present in the sample. Some amounts of Na and Cl were also observed.

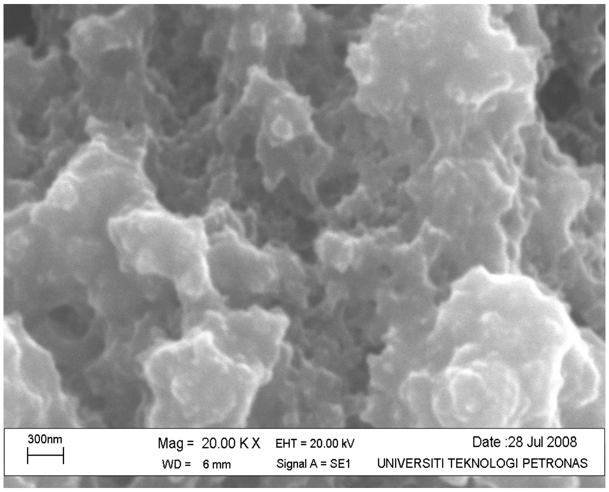


Figure 46: SEM picture of the iron sulfide precipitate at 20X

In the XRD diagram of the FeS sample (Figure-47) peaks of hexagonal nonstoichiometric ferrous sulfide was observed. The cell parameter was a = 6.88 A^0, b = 6.86A^0 and c =28.7 A^0 .The average crystallite size was calculated using Scherer's equation was found to be 911 nm.

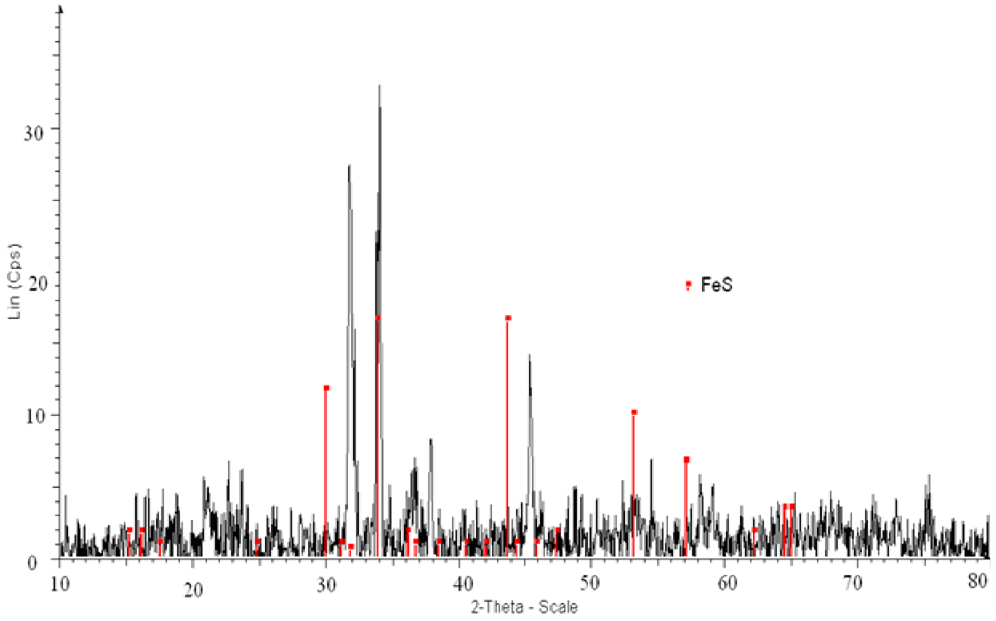


Figure-47: XRD spectrum of the iron sulfide precipitate

In FT-IR spectra of the samples (Figure.48) -OH stretching vibration associated with both inbound and bound water was observed in the region 3787 cm^{-1}, 3552.63 cm^{-1} and 3267.19 cm^{-1}. A diffused peak in the region 800-1400 cm^{-1} with two peaks at 1218.93 cm^{-1} and 991.34 cm^{-1} was assigned to symmetric and asymmetric stretching of Fe-S bond which is an indication of surface activity of the sample.

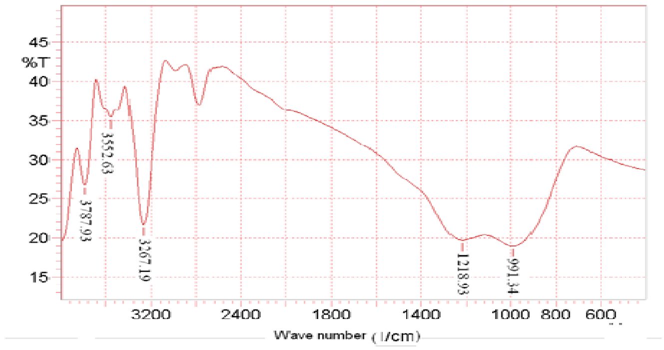


Figure-48: FT-IR spectrum of the iron sulfide precipitate

4.4 Aeration of sulfide in the presence of ultrasonic vibration

Oxidation of sodium sulfide was carried out by aeration in the presence of ultrasonic vibration. The experiment was done using three initial concentrations of sulfides: 600mg/liter and 800mg/lite and 1000mg/liter as shown in the following tables-41, 42 and 43.The effect of ultrasonic vibration on oxidation has been shown in table-41,45 and 46.The effect of air flow rate on oxidation has been shown in table-41,48 and 49.Dissolved oxygen and temperature changes during the oxidation at different initial sulfide concentrations and different ultrasonic vibrations has been shown in the table-44 and 47 respectively.

It was found that oxidation of sulfide produces elemental sulfur and sodium hydroxide. Initial pH of the sulfide solution was 12 or more depending upon the sulfide concentration. The pH of the solution increased gradually with an ultimate value very near equal to 13 which is alkaline pH. Oxidation of 800 ppm took almost 50 minutes. The rate of oxidation was higher at high initial concentration of sulfide. Increasing initial concentration of sulfide increased the time of oxidation of sulfide. It was found that oxidation of 1000 ppm of sulfide takes nearly 60 minutes. The airflow rate and ultrasonic vibration frequency used were fixed, 4l/min and 100% respectively. From the experiment done using the experimental setup and process as shown in Figure-5, the concentration of sulfides dropped over time while the concentration of sulfur increased over time. Oxidation in the presence of ultrasonic vibration frequency of sulfide at different initial sulfide concentrations has been shown in Figure-49. From this experiment, it is clear that the process of removing sulfide ions from wastewater by means of reaction between sulfide ion and dissolved oxygen in the presence of ultrasonic vibrator in wastewater is quite effective. Wastewater during treatment by aeration in the ultrasonic vibrator became turbid due to the formation of elemental sulfur. It was found that the turbidity of solution is higher as high sulfide concentration, which indicated that the rate of formation of elemental sulfur was higher at high concentration of sulfide.

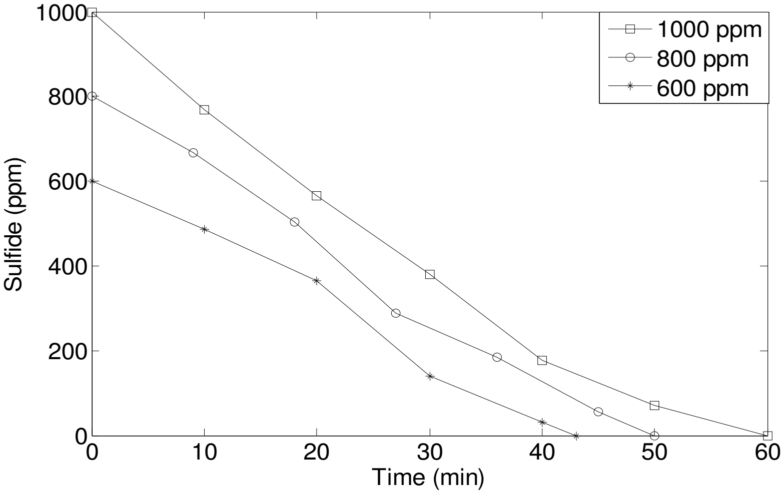


Figure-49.Relationship between time and sulfide oxidized during oxidation at different initial sulfide concentrations.

It was found that higher the atmospheric airflow rates to the opening of the sparger, the faster the sulfide oxidation of the liquid. This is because the higher the atmospheric airflow rates to the opening of the sparger, the larger the concentration of oxygen in the liquid. The larger concentration of oxygen in the liquid would allow more reaction with the excited sulfide ions in the liquid. The increased reaction would will shorten the time to oxidize the sulfides in the liquid.

It was found that the amount of dissolved oxygen maintained constant during the oxidation while the pH of the liquid increased over time. This may be due to the fact that during bubbling of air, the oxygen from the air got dissolved in the solution and the dissolved oxygen reacted with sulfide ions. Under the experimental conditions, the bubbling air supplied oxygen at a sufficiently high rate so that its concentration remained practically constant. The oxygen consumed by the sulfide ions was immediately replenished by absorption from the air bubbles. As sulfide becomes converted to elemental sulfur, the pH increases and tends to move towards the alkaline value of 13. The effect of air flow rate on sulfide oxidation in the presence of ultrasonic frequency has been shown in the Figure-50.

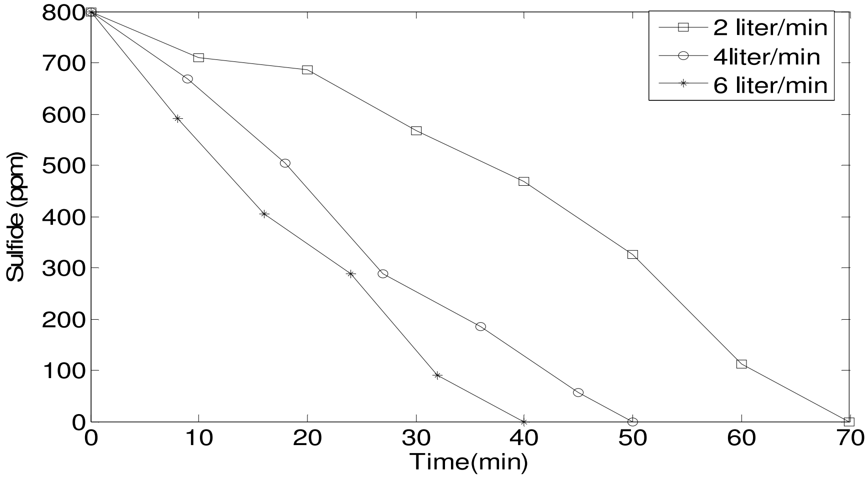


Figure-50: Relationship between time and sulfide during oxidation at different air flow rate

It was found that higher the ultrasonic frequency, faster would be the sulfide oxidation in the liquid. This is because at higher ultrasonic frequency, larger amount of excited sulfide ions were produced. The larger amount of excited sulfide ions in the liquid would allow more reaction with the oxygen in the liquid. Increased reaction would shorten the time to oxidize the sulfides in the liquid. The rate of sulfide oxidation was found to be faster at high intensity of ultrasonic vibration. The effect of ultrasonic frequency on oxidation of sulfide has been shown in the Figure-51.

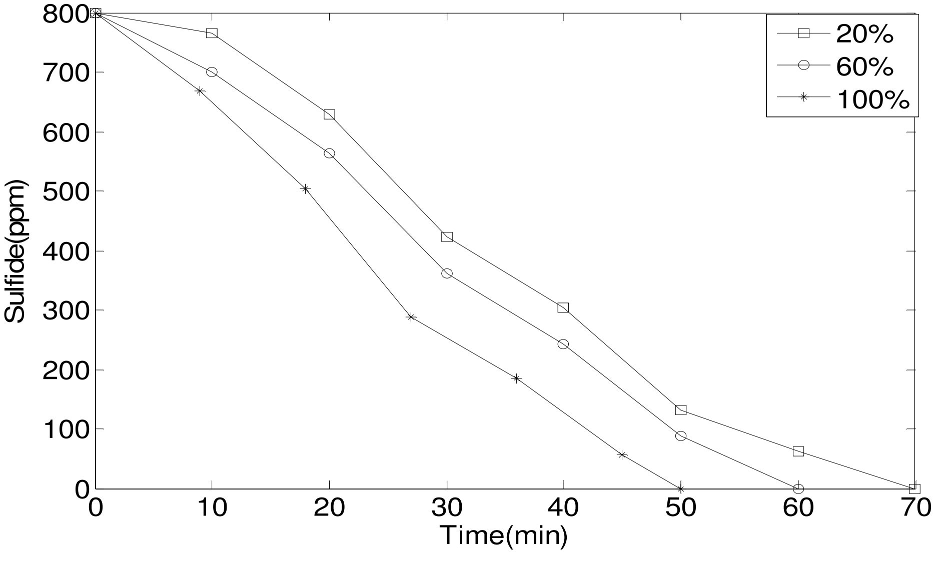


Figure-51.Relationship between time and sulfide oxidized during oxidation at different ultrasonic vibrations

5.4.1. Kinetics of oxidation in the presence of ultrasonic vibration

Power law rate equation for sulfide oxidation has been proposed [O'Brien and Bricker, 1977].

$$r = K_6\,[\text{Oxygen partial pressure}]^{p_1}\,[\text{Sulfide}]^{p_2} \qquad (19)$$

Where K_6 is rate constant, m_1 and m_2 are orders of reaction with respect to oxygen partial pressure and sulfide respectively. A plot of the rate of sulfide oxidation against initial sulfide concentrations on a logarithmic scale at a constant ultrasonic vibration gives the order $p_2 = 0.36$ as shown in figure-52. Thus the order of reaction with respect to sulfide concentration is 0.36.The reaction order with respect to air flow rate was similarly found out by plotting rate of sulfide oxidation against the initial oxygen partial pressure at different air flow rates on a logarithmic scale for constant values of all other parameters as shown in figure-53. The value of p_1 is 0.67 which is order of reaction with respect to oxygen partial pressure. Partial pressure of oxygen was calculated at different air flow rates using ideal gas equation.

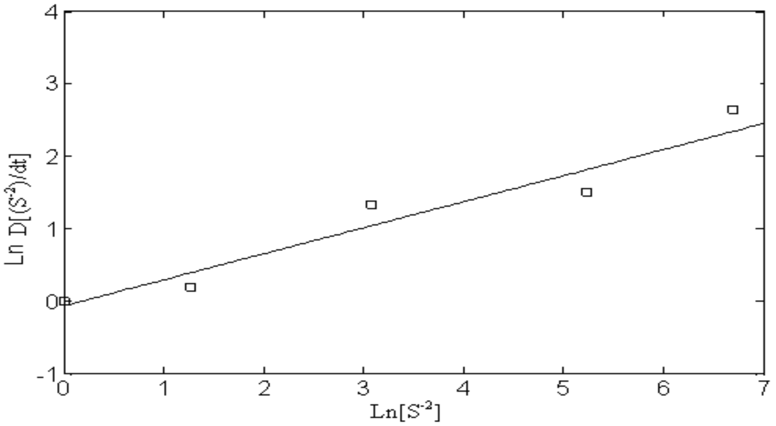


Figure-52.Linear plot of ln[d(S^{-2})/dt] against ln[S^{-2}] on logarithmic scale.

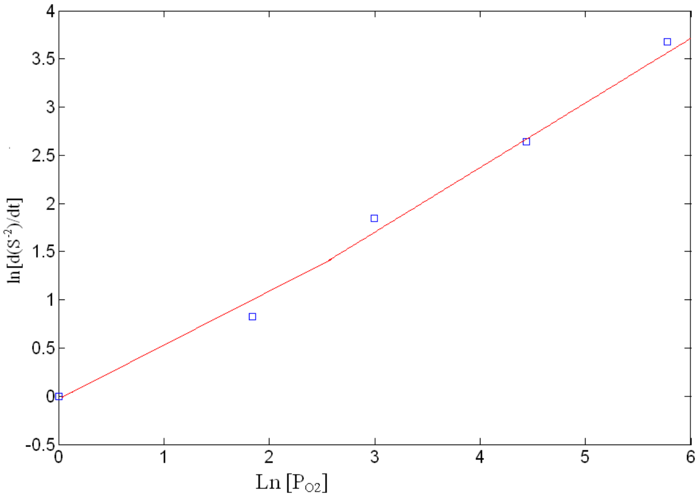
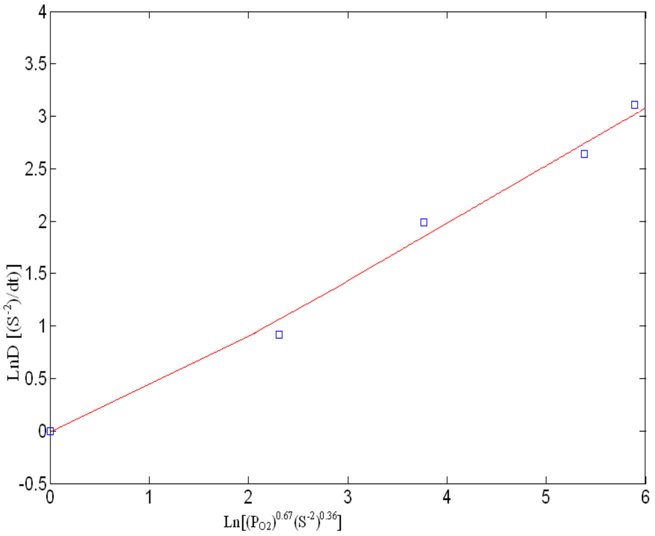


Figure-53: Linear plot between partial pressure of oxygen and rate of sulfide oxidation on logarithmic scale

The reaction rate constant, *k* = 0.55 was determined from the slope of the plot of reaction rate against the product of two concentration terms in Eq. (19) as shown in figure-54.



Fiogure-54: Linear plot of ln[(Air flow rate)0.36 $(S^{-2})^{1.9}$] on logarithmic scale

Chapter 5

SUMMARY AND CONCLUSIONS

Complete removal of sulfide in an aqueous solution was achieved by photo oxidation, catalytic oxidation with hydrogen peroxide, aeration in the presence of ultrasonic vibration and precipitation processes using iron salts. Analysis of the sulfide was done by colorimetric method (methylene blue method). Comparison of the colorimetric and iodometric titration methods were done for sulfide analysis and colorimetric method was found quite satisfactory. Sulfate analysis was done by UV-spectrophotometry method. Photo oxidation of both synthetically prepared and industrial wastewater samples were carried out. The oxidation process was investigated by varying the following variables.

a) Concentration of sulfide
b) Oxygen partial pressure
c) Air flow rate
d) UV light intensity.

The catalytic process is based on the oxidation by H_2O_2 in presence of ferric oxide catalyst, which was synthesized in the laboratory. Rate equations for both sulfide oxidation and sulfate formation were developed. Characterization of the catalyst was done by SEM, EDX, FTIR and XRD. Catalytic oxidation process was investigated by varying the following variables.

i. Concentration of sodium sulfide in the feed water
ii. Catalyst loading
iii. Temperature
iv. Amount of hydrogen peroxide addition.

Sodium sulfide was removed from wastewater by aeration in the presence of ultrasonic vibration. Kinetics of aeration in the presence of ultrasonic vibration was investigated by air flow rate and sulfide concentration.

In precipitation process sodium sulfide was removed by treating sulfidic wastewater with different Fe^{+2}/Fe^{+3} ratio bearing iron salts. The process was investigated by varying the following variables.

1. Concentration of sulfide
2. Iron salts ratio
3. Temperature.

In case of industrial sample the residual sulfide removal was done by aeration. The effect of air flow rate on sulfide removal was checked. Following conclusion from the whole work done on sulfide removal from wastewater was deduced.

i. Rate of sulfide removal by the precipitation of sulfide is higher at high initial sulfide concentration. For relatively high sulfide concentration, most of the sulfide is removed by precipitation and the residual sulfide is removed by aeration.
ii. Rate of sulfide removal is higher at high Fe^{+2}/Fe^{+3} ratio and the sulfide removal reaction follows first order kinetics with respect to sulfide for each ratio of Fe^{+2}/Fe^{+3} added.
iii. Rate of sulfide precipitation is higher at high temperature.
iv. Rate of catalytic sulfide oxidation by hydrogen peroxide was higher at lower initial sulfide concentration and rate of catalytic sulfide oxidation is directly proportional to catalyst loading and hydrogen peroxide addition.
v. At higher temperature rate of catalytic sulfide oxidation by hydrogen peroxide in the presence of ferric oxide catalyst increases significantly.
vi. The iron oxide in nano size with ferric oxide as the major crystalline phase perform the catalytic oxidation for the removal of sulfide ion directly.
vii. The rate of photo oxidation of sulfide is relatively fast at higher concentration of sulfide. The photo oxidation reaction with respect to sulfide concentration follows second order reaction rate.
viii. The rate of formation of sulfate during photo oxidation is fater at high concentration of sulfide. Order of reaction with respect to sulfide is 0.92.
ix. The rate of photo oxidation reaction is faster at high UV light intensity. The kinetics of sulfide reaction was carried out at 4 watts.
x. The photo oxidation reaction time becomes shorter at high air flow rates. The rate of sulfide oxidation is faster at high oxygen partial pressure. Order of reaction with respect to oxygen is 1.4.
xi. Rate of sulfate formation during photo oxidation reaction is faster at high oxygen partial pressure. Order of reaction with respect to oxygen is 1.2.

xii. Rate of reaction for sulfide removal is higher at high sulfide concentration which shows that order of reaction with respect to sulfide concentration is positive.

xiii. It was found that rate of reaction of aeration of sulfide in the presence of ultrasonic vibration is faster at high sulfide concentration and high air flow rates.

The results of this study are expected to be useful for assessment of alternatives and actual remediation of sulfidic wastewater in chemical and allied industries.

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APPENDIX

1. **Standardization of sodium sulfide solution**

A sample of Sodium sulfide has been prepared by dissolving 60% of laboratory grade sodium sulfide in the distilled water. The solution was standardized by both Iodometric titration and colorimetric method. In iodometric titration excess iodine solution was added to the solution which oxidized sulfide to sulfur under acidic conditions. Excess iodine was back titrated with sodium thiosulfate.

In colorimetric method reagents containing potassium dichromate and sulfuric acid were added to the sulfide solution. Color of the solution became blue. The intensity of blue color is proportional to the concentration of sodium sulfide. Monochromatic light having wave length of 665 nm was used in the estimation.

The dissolved sulfide concentration was analyzed by spectrophotometry using Hach 500 UV-vsisble spectrophotom as shown in Figure-56. The result of the instrumental method was checked against the results of classical method. The results were reasonably comparable as shown in Figure.55.

Apparatus as shown in Figure-57. Magnification of images is created by electron beams instead of light waves as in conventional light microscope, which uses a series of glass lenses to bend the light waves. EDX was used for the elemental analysis of ferric oxide and sulfide precipitate formed. It is an analytical technique which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with the electromagnetic radiation. Its characterization capabilities are based on the following fundamental principle. Each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other. To stimulate the emission of characteristic x-rays from a specimen, an high energy beam of charged particles such as electrons or protons, or a beam of x-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell is released in the form of an x-ray. The x-ray released by the electron is then detected and analyzed by the energy dispersive spectrometer. These x-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element form which they were emitted. Picture of the SEM and EDX apparatus has been shown in the Figure-3. SEM and EDX analysis of ferric oxide catalyst and precipitate formed during precipitation were done by using model LEO SUPRA 50 FESEM of SEM and EDX.

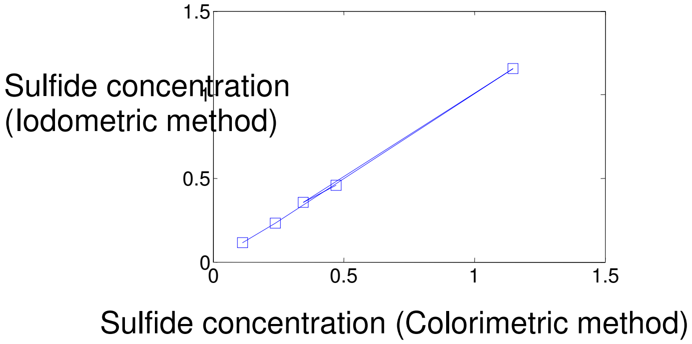

Figure-56.Photograph of the Hach DR-5000 UV-Visible spectrophotometer used in the experiment.

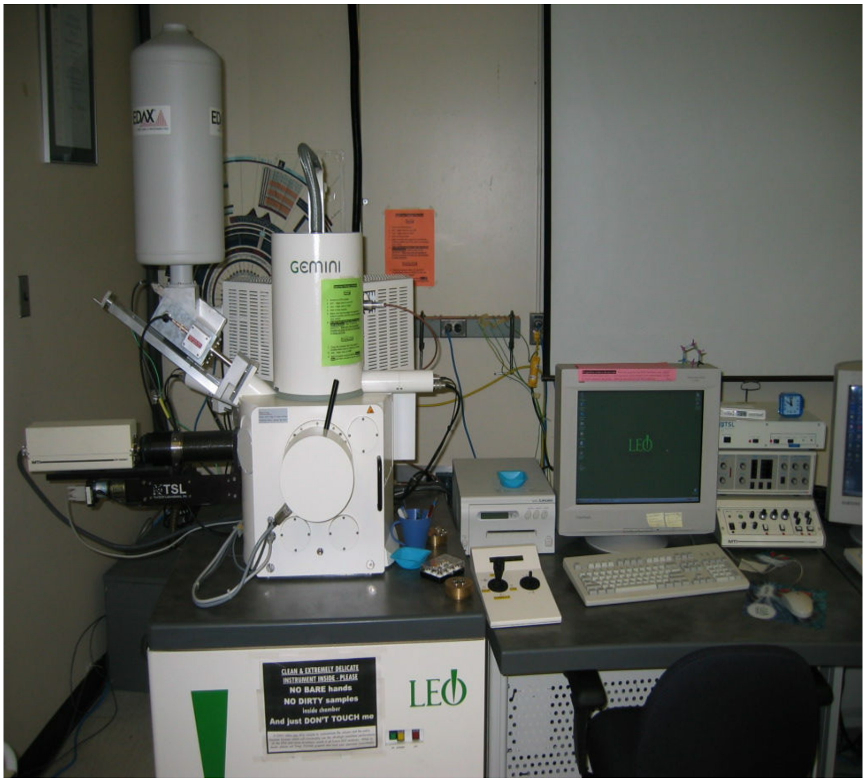

Figure-57: Photograph of Scanning Electron Microscope used in the experiment (model LEO SUPRA 50 FESEM).

FT-IR analysis of the ferric oxide and precipitate formed were done by using Perkin-Elmer apparatus (Model number = Spectrum one). Photograph of the FT-IR apparatus has been shown in the Figure-59.

The XRD analysis of the catalytic and precipitate formed were carried out with BRUKER apparatus (Model number =D8 ADVANCE).Picture of the XRD apparatus has been shown in the Figure-58.

Thermo gravimetric analysis (TGA) was used to evaluate the surface degradation temperature of Ferric oxide. The TGA used in the present analysis is from Pekin Elmer (model Pyris-1) TGA and is shown in Figure-60. This instrument simply measures change in weight as a function of temperature for the sample heated in nitrogen atmosphere.

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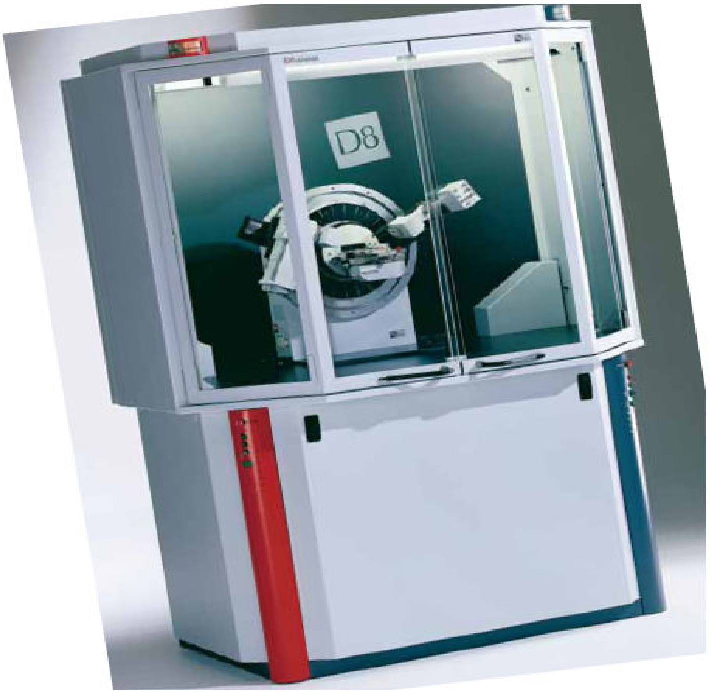

Figure-58: Photograph of the XRD BRUKER apparatus (Model number =D8 ADVANCE) used in the experiment

Figure-59: Photograph of the FT-IR from Perkin-Elmer (Model number = Spectrum one) used in the experiment.

2. Linearization of Rate Equations

(a)Photo oxidation of Sulfide:

$$r = K_1\ [\text{Oxygen}]^{m1}\ [\text{Sulfide}]^{m2} \qquad (12)$$

Taking natural log on both sides

$$\ln(r) = \ln(K_1\ ) + m_1 \ln[\text{Oxygen}] + m_2 \ln[\text{Sulfide}]$$

(b)Catalytic Oxidation by hydrogen peroxide:

$$r = K_3\ [\text{Sulfide}]^{x1}\ [H_2O_2]^{x2}\ [\text{Cat}]^{x3} \qquad (14)$$

Taking natural log on both sides

$$\ln(r) = \ln(k_3) + x_1\ln[\text{Sulfide}] + x_2\ln[H_2O_2] + x_3\ln[\text{Cat}]$$

(c) Precipitation Kinetics: $r = K_4\,[\text{Sulfide}]^{z1}$ (18)

Taking natural log on both sides

$$\ln(r) = \ln(K_4) + z_1\ln[\text{Sulfide}]$$

(d) Aeration in the Presence of Ultrasonic Vibration:

$$r = K_6\ [\text{Oxygen partial pressure}]^{p_1}\ [\text{Sulfide}]^{p_2} \qquad (19)$$

Taking natural log on both sides

$$\ln(r) = \ln(K_6) + p_1\ln[\text{Partial pressure of Oxygen}] + p_2 \ln[\text{Sulfide}]$$

ACHIEVEMENTS

(1) Patent

(i) Binay k. Dutta, **Naveed Ahmad** and Putri Nazarul. “Removal of dissolved sodium sulfide from wastewater by air oxidation in the presence of UV radiation”. Malaysian patent (PI20090321) Jan.2009.

(2) Journals submitted

(a) **Naveed Ahmad**, Saikat Maitra ,Binay k.Dutta and Farroq Ahmad “Catalytic oxidation by hydrogen peroxide” Journal of Environmental Sciences (Elsevier).Accepted for publication 2009.

(b)) **Naveed Ahmad**, Saikat Maitra ,Binay k.Dutta and Farroq Ahmad **“**A new approach for the remediation of sulfidic wastewater using iron salts and aeration” Journal of Chemical Engineerin and Processing. Communicated for publication.

(3) Conferences accepted for presentation

(i) **Naveed Ahmad**, Lintang and Saikat Maitra “Removal of sodium sulfide from wastewater by aeration in the presence of ultrasonic vibration”. Accepted for presentation in the International Conference on Water Resources (May 2009) Langkawi (Malaysia).

(ii) **Naveed Ahmad** and Saikat Maitra. “Removal of sodium sulfide from wastewater by oxidation process in the presence of nano ferric oxide catalyst”. Accepted for presentation in CHEMICA Perth (Australia) October 2009.

(4) Distinction

The patented work has got gold medal in Geneva Innovation Exhibition April, 2009.