



PRETREATMENT OF WASTE ACTIVATED SLUDGE BY SOLAR PHOTO-FENTON PROCESS

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ABSTRACT - In recent years, increased attention has been given to minimization of waste sludge in wastewater treatment process. Many conventional methods are available for Pretreatment of the Waste Activated Sludge viz, Thermal, Chemical, Mechanical, and Biological. Thermal pretreatment requires of a considerable amount of heat to preheat the sludge feedstock, Ultrasonication is the most powerful method to disrupt cell walls, but power consumption becomes a serious drawback (Weemaes&Verstraete, 1998). Other mechanical methods such as grinding and high pressure homogenization are less effective and do not require chemicals or heat, but consume more power and also need longer time periods and are not cost effective. The Solar photo-Fenton reaction, which is one of advanced oxidation processes (AOPs), offers a promising technology for minimization of excess sludge. In AOPs, hydroxyl radicals generated in aqueous solution by Fenton and photo-Fenton reactions are responsible for the degradation of organic pollutants. The experiment is conducted in a Solar Photo-Fenton reactor, the waste activated sludge which is generated from the sequential batch reactor, ferrous sulphate, and hydrogen peroxide are added and exposed to the sunlight. The Sludge is treated within one to six hours of exposure. This study assessed the effect of Fenton's reagent treatment of waste activated sludge. The operating parameters viz., pH, ferrous iron concentration and hydrogen peroxide were optimized as 3, 40mg/L and 4g/L. SCOD and TCOD were 380 mg/L and 1700 mg/L at 4 hr Contact time. The effects of the three critical factors viz., pH, ferrous iron concentration and hydrogen peroxide for pretreatment of waste activated sludge were simulated and evaluated using Response Surface Methodology (RSM). This methodology has shown to be a valuable tool to model complex process such as the light - enhanced Photo-Fento reaction and to achieve optimum experimental parameters at minimal cost. Fenton's reagent addition achieved 22.35% COD Solubilization at only 4 hrs contact time.

Key Words: waste activated sludge, fenton-photo fenton, response surface methodology

I INTRODUCTION

1.1 GENERAL

Sludge production is an avoidable problem arising from the treatment of wastewater. The sludge

remained after municipal wastewater treatment contains considerable amounts of various contaminants and if is not properly handled and disposed, it may produce extensive health hazards. Treatment and disposal of an excess sludge in a biological wastewater treatment system requires an enormously high cost which accounts for approximately 35–60% of the whole operation cost of a wastewater treatment (Neyens et al., 2003) and they are the source of many serious troubles due to their large volume, tendency to putrescibility and bacteriological hazard. Land application or agricultural use of sewage sludge is highly debated, and the landfilling of sewage sludge is now restricted. And an incineration is quite expensive. Moreover the conventional disposal methods of landfilling or incineration cause secondary pollution problems. The cost for sludge treatment is highly dependent on the volume and water content of the produced sludge. Therefore, interest in methods to reduce the volume and mass of excess sludge has been increased.

1.2 ACTIVATED SLUDGE PROCESS (ASP)

This is the most common and oldest biotreatment process used to treat municipal and industrial wastewater. Typically wastewater after primary treatment is treated in an activated sludge process based on biological treatment system comprising aeration tank followed by secondary clarifier. The aeration tank is a completely mixed or a plug flow (in some cases) bioreactor where specific concentration of biomass (measured as mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS)) is maintained along with sufficient dissolved oxygen (DO) concentration (typically 2 mg/L) to effect biodegradation of soluble organic impurities measured as biochemical oxygen demand (BOD₅) or chemical oxygen demand (COD). About 30% of the secondary sludge produced is returned to the aeration tanks to assist with the biological process of sewage treatment. The remaining 70% (excess biomass - produced during the biodegradation process) is wasted to the sludge handling and dewatering facility. The treatment and final disposal of the produced primary and secondary excess sludge takes up a significant part of the material- and financial resources of the waste water treatment plant. The excess sludge from an activated sludge process has three undesirable aspects:

1) Biological instability: the excess sludge is putrescible due to the high fraction of biodegradable organic matter and enters into decomposition within hours after the interruption of aeration



2) the hygienic quality of the excess sludge is very poor: a very large variety of viruses, bacteria and other pathogens (protozoa, amoebae, helminth eggs) are present

3) the suspended solids concentration in the excess sludge is low: in the range of 3 to 50 g/L, depending on the origin of the sludge and on the type of solid-liquid separation process used, resulting in a large volume of excess sludge to be handled.

1.3 GENERATION OF SLUDGE AND ITS CHARACTERISTICS

Specific sludge production in wastewater treatment varies widely from 35 to 85 g dry solids per population equivalent per day ($\text{gTS PE}^{-1} \text{d}^{-1}$). The production of primary sludge is related to the amount of settleable solids in raw wastewater whose solids content is typically of $50\text{-}60 \text{ gTSS PE}^{-1} \text{d}^{-1}$ or $110\text{-}170 \text{ gTSS/m}^3$ of treated wastewater (Tchobanoglous *et al.*, 2003).

Organic matter is oxidised by heterotrophic microorganisms to produce H_2O and CO_2 in the process known as *catabolism*. This process requires the availability of an electron acceptor which may be oxygen or nitrate and lead to the production of energy as ATP. This energy is then used by microorganisms to grow forming new cellular biomass and to guarantee maintenance functions such as the renewal of cellular constituents, maintenance of osmotic pressure, nutrient transport and motility in the process called *anabolism*.

Simultaneously biological decay of cellular biomass occurs, which creates two fractions (i) biodegradable particulate COD (X_S) and (ii) endogenous residue considered as inert particulate COD (X_P), which accumulates in the system. The X_S fraction is subjected to hydrolysis process and is further oxidised to generate new cellular biomass (*cryptic growth*), while the endogenous residue (8-20%) remains and accumulates in the sludge. A simplified scheme of these processes leading to sludge accumulation in a biological treatment of influent wastewater is indicated in the Figure 1.2.

Conventional characterisation parameters can be grouped in physical, chemical and biological parameters. Physical parameters give general information on sludge processability and handlability, Chemical parameters are relevant to the presence of nutrients and toxic/dangerous compounds, so they become necessary in the case of utilisation in agriculture, and Biological parameters give information on microbial activity and organic matter/pathogens presence, thus allowing the safety of use to be evaluated.

The sludge characteristics which are important to know strictly depend on the handling and disposal methods adopted. The most important parameters yielding basic information are particle size distribution, water retention and rheological properties.

1.4 IMPACTS OF SLUDGES ON ENVIRONMENT

Methods of sewage sludge disposal, such as incineration and uncovered landfills, may contribute to

global warming by releasing carbon dioxide and methane. Sewage sludge with high concentrations of certain organic and metal pollutants may pose human health problems when disposed of in sludge-only landfills or simply left on the land surface, if the pollutants leach from the sludge into the ground water. Therefore, the pollutant concentration may need to be limited or other measures such as impermeable liners must be taken to ensure that ground water is not contaminated. For the incineration of sewage sludge, municipalities must take sufficient measures to control the emissions from sewage sludge incinerators. Otherwise, particulates, heavy metals, toxic organic compounds, and hydrocarbons will add to a community's air pollution problems. Ocean dumping of sludge, which Congress banned after 1991, may result in the destruction of biota that influence the balance between oxygen and carbon dioxide. In ocean disposal, certain pollutants often associated with municipal sludge, including mercury, cadmium, and polychlorinated biphenyls, can bioaccumulate. High levels of these pollutants can interfere with the reproductive systems of certain marine organisms, may produce toxic effects in aquatic life, or may present public health problems if individuals eat contaminated fish and shellfish.

1.5 SLUDGE MANAGEMENT

Biological treatment of wastewater performs excess biological solids due to the growth and multiplication of bacteria and other microorganisms in the system. The quantity of excess sludge generated in the STP is dependent on various factors including the BOD concentration, MLSS levels, temperature etc. The F/M loading rate is however the factor which chiefly determines the amount of excess solids produced. A typical figure for use in India is between 0.20 to 0.25 times (on dry mass basis), kg of BOD removed in the aeration tank, in extended aeration systems with low F/M. Since the excess sludge is available in slurry form from the sludge recirculation line, the slurry consistency may be taken to be between 0.8 to 1.0 %.

The excess biomass thus produced needs to be bled out of the system, and disposed off efficiently. This is a five-step process: sludge removal, storage, conditioning, dewatering and disposal.

1.6 SLUDGE PRETREATMENT TECHNOLOGIES

A number of treatability studies of sludge from activated sludge process have been done to treat the sludge up to a sufficient degree, which render it safe and comply with regulatory standards. Even though a lot of treatment methods are available with their own advantages and disadvantages, advanced oxidation process is more promising and effective technology.

1.6.1 Solar Photo Fenton Process

The Fenton reaction has been used to improve the dewatering of sludge. The application of the photo-Fenton reaction to minimization of excess activated sludge is based on the idea that part of activated sludge is



mineralized to carbon dioxide and water while part of sludge is solubilized to biodegradable organics, which can be biologically treated.

It can be expected that the photo-Fenton reaction destructs bacterial cell membranes, discharges biomass particulates and transform them into a soluble composition such as proteins, lipids and polysaccharides (Liu et al., 2001).

1.7 NEED FOR THE PRESENT STUDY

The sludge resulting in the production of extremely large volumes of residual solids, and significant disposal costs. Thereby, the conventional method leads to water pollution problem into solid waste disposal problem. The main alternative methods for sludge disposal are landfilling, land application and incineration. Incineration is quite expensive and land application (or agricultural use) is subject to reservations from farmers and consumers. There is therefore, a growing interest in developing technologies to reduce the wastewater sludge generation. Aerobic or anaerobic digestion of waste activated sludge is often slow due to the rate limiting cell lysis step and extracellular polymeric substance (EPS) is relatively recalcitrant to both the digestion process by nature. Indeed, various studies have reported EPS as 30-50% biodegradable (Wang et al., 2007). In a conventional mesophilic anaerobic digestion process with a HRT of 20 days, conversion of organics to gas is typically 25-60% (Parkin et al., 1986, Bhattacharya et al., 1996) with the lower performance on long-sludge age activated sludges. The goal of pretreatment is to improve this either by increasing the rate, or the inherent degradability of the material. Solar Photo-Fenton pretreatment has been studied in order to increase the rate of the process and also improve the aerobic biodegradation of solid wastes.

1.8 OBJECTIVES OF THE STUDY

- To minimize the waste activated sludge by Solar Photo-Fenton Pretreatment Process.
- To generate and characterize TS, COD of waste activated sludge.
- To study the effect of major operating parameters on Solar Photo-Fenton Pretreatment process viz., pH, Fe(II), H₂O₂, contact time for the maximum and minimum organic content present in the sludge.
- To arrive the kinetics of Sludge pretreatment system.
- Design of Solar Photo-Fenton pilot scale processes for Sludge Pretreatment system.
- Cost analysis for solar photo Fenton processes for Pretreatment of Sludge.

II MATERIALS AND METHODS

In this present study, the systematic studies were done to pretreat the waste activated sludge with solar photo-Fenton process. The pretreatment study of waste activated sludge by solar photo-Fenton process was carried out at the terrace of the Anna University of Technology,

Tirunelveli. The various materials used and the methodology adopted for the studies are described in this chapter.

2.1 COLLECTION AND CHARACTERIZATION OF WASTE ACTIVATED SLUDGE

Waste activated sludge samples were obtained from the returnline of the secondary sedimentation tanks of a municipal WWTP in Trivandrum. Samples were stored at 4 °C prior to use. Sludge will be analyzed to determine the required characteristics of sludge such as pH, TSS, COD and MLSS as per standard methods using APHA manual.

2.2 EXPERIMENTAL SETUP FOR LABORATORY-SCALE STUDIES ON SOLAR-FENTON PROCESS

In Biological Process, the operating parameters such as COD, SRT, HRT and MLSS were characterized and the effect of sludge yield was studied. Then the generated Sludge from the sequential batch reactor (fig 2.1) was sent to the Solar Photo-Fenton reactor (fig 2.2) where the volume of the reactor was 2L and the working volume was 500ml. The operating parameters such as pH, Fe²⁺, H₂O₂, contact time were to be optimized in Fenton process. The experiments were conducted from 11.00 p.m to 3.00 p.m from January to April. The sample was taken from reactor at every 1 hr and analyzed the SCOD, MLSS and the parameters were optimized.



Fig.2.1 Sequential Batch Reactor to generate WAS



Fig 2.2 Experimental setup for solar photo Fenton process



2.2.1 Effect of Operating Conditions in Solar Photo-Fenton Pretreatment Process

The effects of operating parameters such as pH, Fe²⁺, H₂O₂ and contact time were determined and the various operating parameters were analyzed and optimized.

The experiments were conducted varying the pH in the range of 2-4 and the reaction was carried out for 0 to 4 hrs with the dosage of Fe²⁺ - 40mg/L and H₂O₂ - 4 g/L. The sample was taken for every 1 hr. After fixing the optimized pH other parameters were changed and studied. The experiment was conducted by varying the H₂O₂ in the range of 2 – 4 g/L. Hydrogen peroxide concentration was optimized by varying its value with constant Fe²⁺. The Effect of Fe²⁺ concentration on the COD removal was studied. During the optimization of Fe²⁺, the concentration of Fe²⁺ varies in the range of 20 to 40mg/L with the optimum dosage of H₂O₂ as 4 g/L. The sludge sample of volume 1L was taken in the reactor. H₂O₂ and FeSO₄ was added and mixed well. The solar Fenton reactions were carried under strong solar radiation from 12.00 to 1.00pm. The Effect of contact time was analyzed by withdrawn the sample from solar Fenton reactor at different time intervals 0-4 hr and measured soluble COD and MLSS.

2.2.2 Optimization of Solar Photo-Fenton for Pretreatment of Waste Activated Sludge by Response Surface Methodology

In order to describe the relation between a system response and input factors typically a mathematical model is formulated. The combination of experimental design and formulation of a mathematical model to yield a quantitative description of the response over a whole experimental region in a system with n continuous input factors is called Response Surface Methodology (RSM), because the system response can be described by a continuous surface in the n dimensional factor space [Box et al., 1978]. Usually, the input factors are scaled in such a way that the minimum value of the respective factor of the investigated region is -1 and the maximum value is +1.

Table 2.1 Experimental range and levels of the independent test variables

Variables	Ranges and levels		
	-1	0	1
Initial pH (A)	2	3	4
Fe ²⁺ (B) (mg/L)	35	40	45
H ₂ O ₂ (C) (g/L)	45	50	55

A class of three level of complete Box-Behnken design for the estimation of parameters in a second order mode was developed by Box-Behnken. The actual design of experiments is listed in Table 2.1. The three significant independent variables A, B, C and the mathematical relationship of the response Y on these variables can be

approximated by a second-degree polynomial equation (Douglas 2004).

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} A B + \beta_{13} A C + \beta_{23} B C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \quad (3.1)$$

The regression equation obtained after analysis of variance gives the level of COD solubilization as a function of different concentration of Fe²⁺, pH and H₂O₂. Regression mode containing 3 linear (A, B and C), 3 quadratic (A², B² and C²) and 3 interaction terms plus 1 block term was employed by using the design expert. The design was performed because relatively few experimental combinations of the variables were needed to estimate potentially complex response functions. A total of 17 experiments were necessary to estimate the 10 coefficients of the model using multiple linear regression analysis. The above equation was solved by using the design expert (Stat - Ease Inc. version 7) to estimate the response of the independent variables. The maximum predictable response for COD Solubilization was also obtained.

2.2.3 Treatability Studies

Treatability studies on Solar Photo-Fenton was studied under optimum conditions at pH 3, Fe²⁺ dosage of 40 mg/L, H₂O₂ dosage of 4 g/L for high solubilization of COD of Waste activated sludge and the volume of sludge reduction occurred by the minimization of MLSS value and then kinetics was studied based upon the treatment processes.

2.2.4 Design of Pilot-Plant System and Treatment Cost Estimation

The design of Solar Photo-Fenton system was done for treating 1.25 x 10⁻³ m³/ min containing inlet sludge concentration of 4500 mg/L. Design was done based on the reactor configuration, Rate constant, i.e., kinetics of the process, Desired destruction level or destruction and removal efficiency (DRE). Total cost of the treatment plant was calculated by including capital cost and operating cost. The capital cost includes cost of reactor, storage and settling tanks, piping, fittings, pumps, blowers, controls, installation, auxiliary and capital contingency. The Operational and Maintenance (O & M) cost includes catalyst, oxidant, pre and post-treatment, filters, energy, and maintenance.

III RESULTS AND DISCUSSION

The effect of the Solar Photo-Fenton Process in treating Waste Activated Sludge was studied. The parameters viz., pH, TCOD, SCOD and MLSS were analyzed. Then the Sludge was treated with the Fenton's reagent and exposed to solar irradiation in the lab scale using solar reactors and the operating parameters namely effect of pH, Fe²⁺, H₂O₂ and contact time were optimized. The results obtained are discussed below.

3.1 CHARACTERIZATION OF SLUDGE



Table 3.1 shows the initial Characteristics of the Sludge. It was observed that the concentration of Sludge was 42, 843 mg/ L, SCOD and TCOD were 650 mg/L and 50,350 mg/L respectively.

Table 3.1 Initial Characterization of the Sludge

Sl.NO	PARAMETERS	VALUE
1	pH	7
2	MLSS (mg/L)	42843
3	SCOD (mg/L)	650
4	TCOD(mg/L)	50350

3.2 STUDIES ON SOLAR PHOTO-FENTON PROCESS: EFFECTS OF OPERATING PARAMETERS

The studies had been carried out in order to study the effects of operating parameters such as pH (2-5), Fe^{2+} dosage (20-50 mg/L), H_2O_2 dosage (2-5 g/L), contact time (4 h) for SCOD and MLSS . To study the effects of operating parameters, the experiments were conducted under the conditions of pH 3, Fe^{2+} dosage 40mg/L and H_2O_2 dosage 4 g/L.

3.2.1 Effect of Solar Photo-Fenton Process

In order to study the effect of solar irradiation and Fenton Process, four sets of experiments were conducted viz. Only H_2O_2 (without Fe^{2+}), Only Fe^{2+} (without H_2O_2), Only UV irradiation (solar) and photo-Fenton (solar/ Fenton). The results of the experimental studies were depicted in following figures.

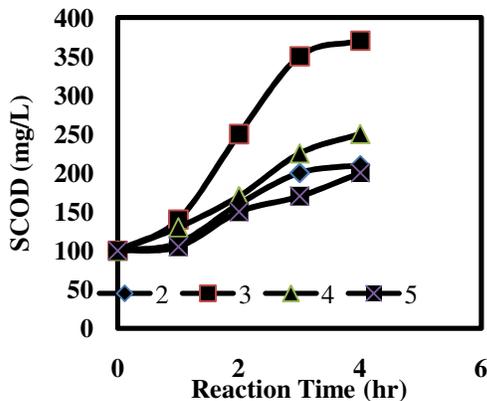


Figure 3.1 Optimization of pH based on SCOD

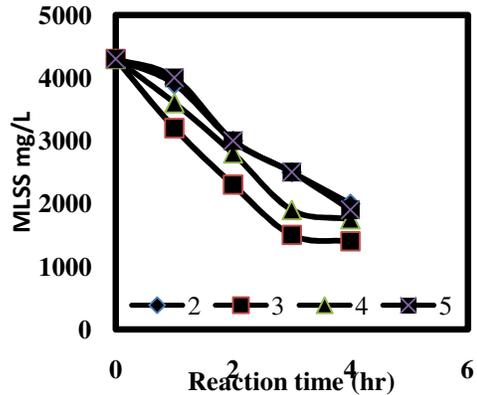


Fig 3.2 Optimization of pH based on MLSS

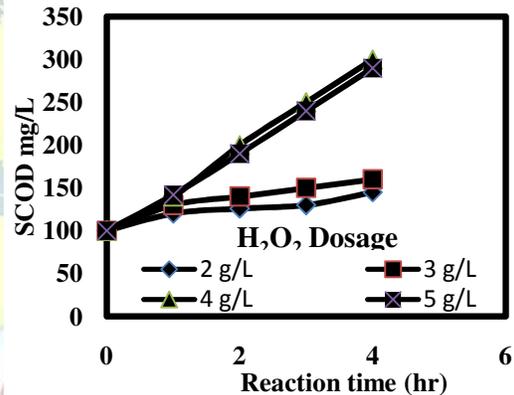


Fig 3.3 Optimization of H_2O_2 dosage based on SCOD

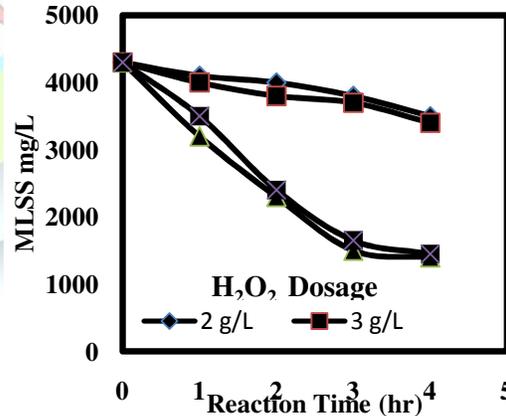


Fig.3.4 Optimization of H_2O_2 dosage based on MLSS

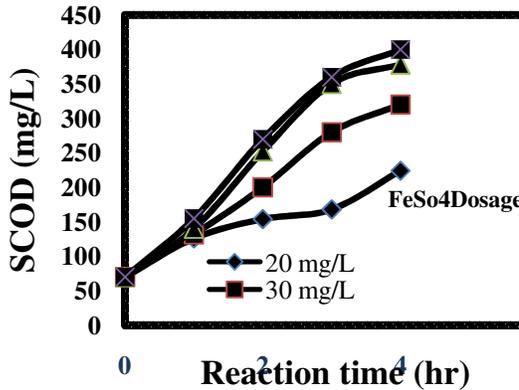


Fig 3.5 Optimization of Ferrous Sulphate dosage based on SCOD

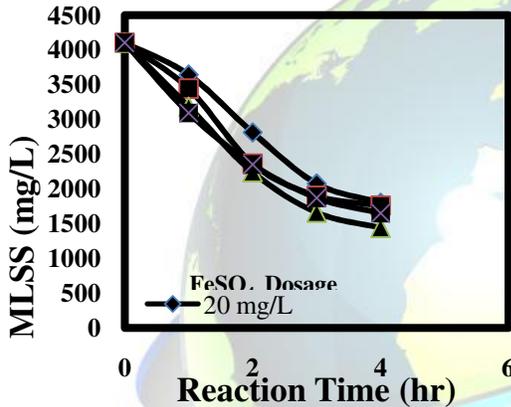


Fig 3.6 Optimization of Ferrous Sulphate dosage based on MLSS

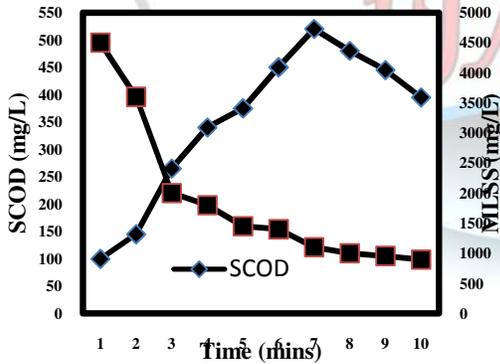


Fig 3.7 Optimization of Contact Time

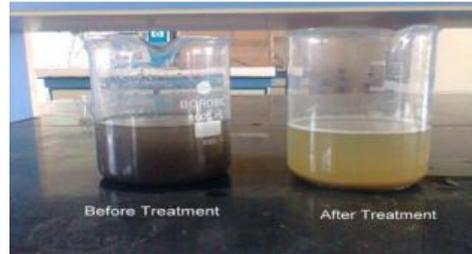


Fig3.8 Change in color of sludge suspension

The experiments were performed in the pH of 2,3,4 and 5 by maintaining other process parameters. Fig 3.1, 3.2 shows, at the initial pH 3.0 being optimal for the photo-Fenton reaction, COD increased until $t = 4$ h. The solution pH slightly increased during the reaction. When the solution pH was actual (pH 7), SCOD increased up to 2 h and decreased very gradually with reaction time. The pH has a significant role determining the efficiency of Fenton and photo-Fenton oxidation. Except as otherwise specified the initial pH of the solution was adjusted to 3 which is the optimal value for the (photo) Fenton reaction. Initial concentration of H_2O_2 plays an important role in the photo-Fenton reaction. Fig. 3.3 and 3.4 depicts effects of the initial H_2O_2 concentration on sludge reduction at different H_2O_2 concentrations (2–4 g /L). For the initial H_2O_2 concentrations of 2 and 4 g /L, the mineralization of organic matters occurred as well as the destruction of cell walls. The increase in initial H_2O_2 concentration was found to enhance the sludge disintegration rate.

In Fig. 3.5 and 3.6, the effect of Fe dosage on the degradation of microorganisms is presented. The experiments were conducted in the Fe ion concentration range of 20–50 mg/L for fixed initial concentrations of sludge and H_2O_2 of 4000 mg/L and of 4 g/L, respectively and the initial solution pH of 3. When the Fe ion concentration was 20 mg/L, the COD increased. When the Fe dosage was 40 mg/L, the COD increased and reached at the maximum at $t = 4$ h and the SCOD increased more quickly as compared with other Fe dosages. Fig. 3.8 illustrated the dark brown color of the sludge suspension before the treatment changed to pale gray after 12 h treatment. The MLSS decreased from the initial value of 4500–895 mg/L after 9 h (fig 3.7) of photo-Fenton reaction with the initial H_2O_2 concentration of 4 g /L. First the decrease in MLSS occurred rather significantly and then sluggishly. Ferrous ion catalyzed H_2O_2 to form OH radical quickly in the first stage of reaction.

3.3 Optimization Of Solar Photo-Fenton Process For The Pretreatment Of Waste Activated Sludge by Response Surface Methodology

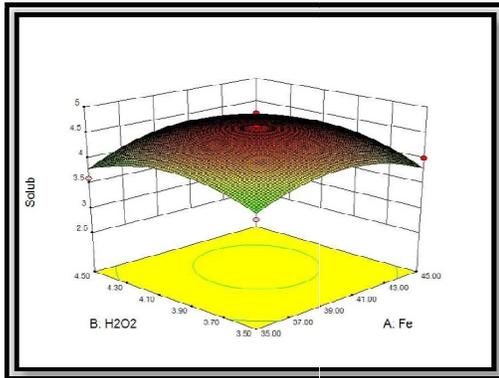


Fig 3.9 Response surface optimization of COD Solubilization vs Fe and H₂O₂

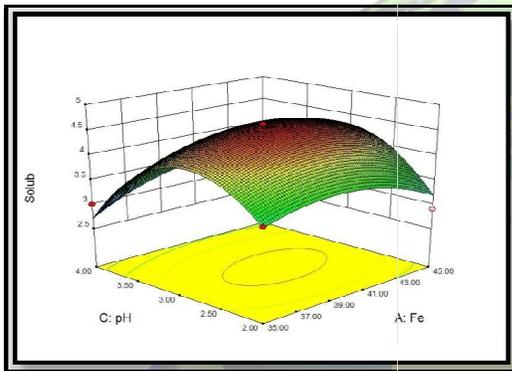


Fig 3.10 Response surface optimization of COD Solubilization vs Fe and pH

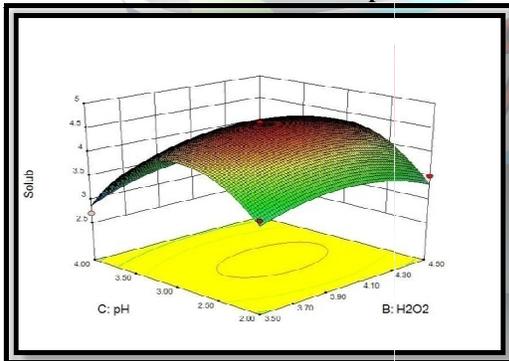


Fig 3.11 Response surface optimization of COD Solubilization vs. H₂O₂ and pH

The application of RSM offers on the basis of parameter estimate, an empirical relationship between the COD Solubilization efficiency and the test variables under consideration. Fig 3.9, 3.10, 3.11 shows the results obtained from the optimization of variables using Response Surface Methodology. The response variable and the test variables are related by the following quadratic expression (Equation 3.1).

$$Y = 4.62 + 0.082A + 0.072B - 0.16C + 0.085AB + 0.23AC + 0.11BC - 0.38A^2 - 0.38B^2 - 1.06C^2 \quad (3.1)$$

where Y is the response, which is the COD Solubilization efficiency expressed in mg/Wh and A, B and C are the coded values of Fe, H₂O₂, and pH respectively.

CONCLUSION

Waste activated sludge samples were obtained from the return line of the secondary sedimentation tanks of a municipal WWTP in Trivandrum. The pretreatment study of waste activated sludge by solar photo-Fenton process was carried out at the terrace of the Anna University of Technology, Tirunelveli. Based on the review of literature, the methodology of the present study is formulated as solar photo-Fenton's process. While many chemical oxidants have been used in the recent past Fenton's reagent which uses hydrogen peroxide as oxidant and ferrous ions as catalyst to generate hydroxyl radicals is highly efficient in treating waste activated sludge. This process will give higher degradation efficiency of the sludge in the presence of sunlight. Sunlight is an abundant natural energy source.

Solar Photo-Fenton process can make use of sunlight instead of artificial light, which reduces the operating costs and it is eco-friendly to the environment. Being India is a tropical countries and hence solar Fenton process is highly suitable and a promising process. Solar Photo Fenton process is relatively inexpensive, non-persistent and unlikely to be a health hazard if used properly. Advanced oxidation processes (AOP) have become the most widely used treatment technologies for organic pollutants not treatable by conventional technologies due to high chemical stability and/or low biodegradability of such pollutants. These processes involve generation and subsequent reaction of hydroxyl radicals (OH). This study assessed the effect of Fenton's reagent treatment of waste activated sludge. The operating parameters viz., pH, ferrous iron concentration and hydrogen peroxide were optimized as 3, 40mg/L and 4g/L. The sludge generated from the sequential batch reactor is treated with Fenton's reagent with solar irradiation for four weeks. Results showed SCOD and TCOD were 380mg/L and 1700 mg/L at 4 hr Contact time.

The effects of the three critical factors viz., pH, ferrous iron concentration and hydrogen peroxide for pretreatment of waste activated sludge were simulated and evaluated using Response Surface Methodology (RSM). This methodology has shown to be a valuable tool to model complex process such as the light-enhanced Photo-Fenton reaction and to achieve optimum experimental parameters at minimal cost. Results showed the viability of the Fenton process in the pretreatment of sludge. In summary, evidence showed that Fenton's reagent addition achieved 22.35% COD Solubilization at only 4 hrs contact time. It is a time consuming process and the cost of the treatment is less when compare to other conventional pretreatment process. The main advantage of Advanced Oxidation Process is simplicity, good sludge reduction, and easy



onsite treatment. Results obtained from this research indicated that the solar photo-Fenton treatment could be a suitable pretreatment method for enhancing biodegradability of sludge treated in the solar photo fenton system.

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