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ENHANCEMENT OF WASTE ACTIVATED SLUDGE REDUCTION POTENTIAL BY THERMO-FENTON TREATMENT

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Abstract - *In Global level the number of sewage treatment plants has progressively increased as a sequence of hasty urbanization and firm expansion in human populace. Surplus sludge produced by various treatment plants are of an immense ecological peril due to the presence of unprocessed solids, pathogens and other organic pollutants. The excess sludge produced from wastewater treatment plants in India is an undisputed drawback. The efficiency of Thermo-Fenton treatment was predicted in terms of sludge reduction. The main objective of this study is to increase the efficiency of the pre-treatment within a short period of time. The SCOD and MLSS will be used to determine the efficiency of the pre-treatment. The effect of parameters such as Fe^{2+} / H_2O_2 dosage, time and temperature has been studied.*

Key Words*: *Waste activated sludge, Thermo-Fenton process, Advanced oxidation process, Soluble chemical oxygen demand, Mixed liquor suspended solids

1. INTRODUCTION

Waste Activated Sludge is an environmental related problem due to its composition which includes organics, pathogens and other harmful compounds, which require management. Sludge accumulates as a residue in all sorts of treatment and mostly production process in industry. Sludge comprises of solids and colloids separated from biological and chemical operation units. Activated sludge consists of high rates of chemical, organic and microbial pollutants. If they are not stabilized completely and discharged safely, they will become a potential pollution source, threatening soil and water bodies. Therefore, sludge management is identified as an important issue in wastewater management. Before the final disposal, the WAS must be treated because of its high organic and pathogen microorganism content. The treated sludge can be disposed of by means of land filling and incineration techniques. Disposal by means of land filling leads to groundwater contamination under certain circumstances whereas disposal by means of incineration leads to air pollution problem. Moreover these disposal methods may cause impact to human and environment. However, the sludge management is one of the most difficult and expensive problems in the treatment plants. In recent years, greater attention has been given to minimization of waste sludge in wastewater treatment process.

Dewatering is of paramount importance in the subsequent sludge processing as it reduces sludge volume and, consequently, the cost of disposal of sludge has weighed on management of effluent treatment plants and shortage of a disposal place. However, such sludges are often regarded as difficult to dewater due to the strong hydrophilicity. Therefore, sludge dewatering is still a major challenge for environmental researchers. Treatment and disposal of excess sludge amount to approximately half the entire operating cost for domestic wastewater treatment plants. Research of excess sludge treatment has been extensively carried out and some novel sludge reduction techniques have been proposed. The feature of the latest sludge treatment technology is changing the character of sludge and reducing the quantity of sludge. To alleviate this problem, various methods have been proposed for treatment of sludge. Several methods such as mechanical disruption, thermal hydrolysis, chemical and thermo-chemical hydrolysis, biological hydrolysis and ultrasounds have been developed to reduce the sludge burden.

Current results suggest great potential of the chemical technology in reducing excess sludge production [1]. Advanced Oxidation Process (AOP) is the type of Chemical Oxidation process, refers to a set of chemical treatment procedures designed to remove organic and inorganic materials in waste water by oxidation. Lots of researches have been addressed to this aim in the last decade pointing out the prominent role of a special class of oxidation techniques defined as Advanced Oxidation Processes which usually operate at or near ambient temperature and pressure [2]. AOPs might be used in wastewater treatment for reduction of overall organic content (COD), colour, odour and specific pollutant for sludge treatment.

The Fenton process is a rapidly emerging Advanced Oxidation Process (AOP) adopted for the removal of contaminants in sludge. The utilization of Fenton's reagent is the most effective method to treat because the hydroxyl radicals formed during the reaction of ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2) have the tendency to degrade the organic matter and minimize the excess activated sludge is based on the idea that part of activated sludge is mineralized to carbon dioxide (CO_2) and water (H_2O) while the sludge is solubilised to organics. Equations (1) to (4) detail the oxidation of organic compounds (RH) by Fenton's reagent [3].

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO\bullet \quad (1)$$

$$Fe^{2+} + HO\bullet \longrightarrow Fe^{3+} + OH^- \quad (2)$$

$$HO\bullet + RH \longrightarrow H_2O + R\bullet \quad (3)$$

$$R\bullet + Fe^{3+} \longrightarrow R^+ + Fe^{2+} \quad (4)$$

These reactions generate organic radicals and further oxidation reactions of these radicals with hydroxyl radicals result in complete mineralization of organic pollutants. The major parameters affecting Fenton process are solution's pH, amount of ferrous ions, concentration of H_2O_2, initial concentration of the pollutant and presence of other ions. The main advantage of the process is degrade the organic as well as inorganic pollutants that will lead to high mineralization levels. The degradation efficiency of organic pollutants in the Fenton process depends on operation parameters such as wastewater pH, concentration of Fenton reagent, and initial organic pollutants concentration, of which wastewater pH is a highly important parameter. The Fenton reaction on sludge floc is represented in Fig. 1.

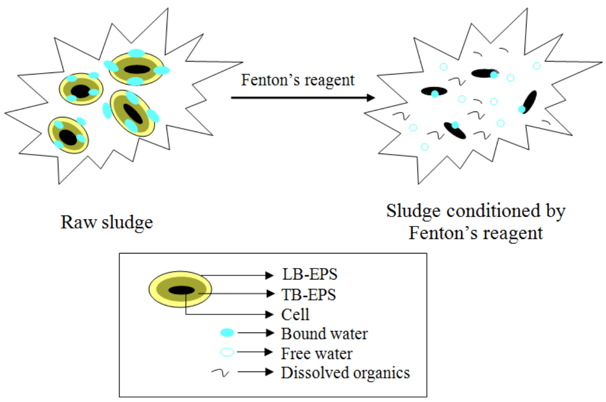

Fig. 1. Fenton reaction on sludge floc

The need for study of the project as to overcome the complex problem involved in the treatment and disposal of sludge produced from conventional wastewater treatment plant. By applying Fenton, sludge disintegration, mineralization & solubilization occur. When the energy requirement for this process is low, the operational cost automatically decreases. As this process has no toxic substances added, no mass transfer limitations due to its homogeneity, it has no effects on the environment. So it is an eco-friendly process. The objectives of this project are (1) to analyze the characteristics of the collected WAS, (2) to optimize the temperature, dosage of Fe^{2+} and H_2O_2 and (3) to study the efficiency of the process under different dosage ratio.

2. MATERIALS AND METHODS

2.1 Collection of sample

Municipal waste activated sludge was collected from the secondary clarifier of a Sewage Treatment Plant of Karakonam Medical College, Kerala. The sludge has been collected in cans and carried to the lab where it was stored at 4°C, for further studies. Initial characteristics of the collected sludge is tabulated in Table 1.

2.1 Thermo-Fenton treatment

The experiment is to be done in the water bath at various temperatures from 50°C to 90°C. Series of experiments will be performed in order to find the optimum operational conditions. 500mL of sludge sample having MLSS concentration of 5000 mg/L was taken in a beaker with a working volume of 1 litre. The sludge pH was first adjusted to the desired pH value by adding sulphuric acid. Then the required amount of Fe^{2+} (0.001 g/g SS to 0.01 g/g SS) and H_2O_2 (1μL to 10μL) was added into the sludge sample and stirred well to enhance the homogeneity of sludge during the reaction. Hydrogen peroxide was then added into the WAS. After the addition of H_2O_2, it was assumed that Fenton reaction was started. The reaction proceeds and the samples were collected from 0 to 60 min. About 5 mL of sample was collected after certain time intervals.

Fig. 2. Experimental setup for Thermo-Fenton process

2.3 Analytical methods

The parameters such as MLSS, SCOD, protein and carbohydrate were observed based on the Standard methods (APHA, 2005). The extent of MLSS reduction and COD solubilization efficiency were calculated by the formula given below:

$$\text{MLSS reduction (\%)} = [(\text{Initial}_{SS} - \text{Final}_{SS}) / \text{Initial}_{SS}] \times 100$$

$$\text{COD solubilization (\%)} = \frac{(SCOD_P - SCOD_i)}{(TCOD_i - SCOD_i)}$$

Table-1: Initial characterization of WAS

S.No	Parameters	Unit	Value
1.	Total Solids	mg/L	12000 ± 100
2.	Total Suspended Solids	mg/L	7000 ± 100
3.	TCOD	mg/L	8000 ± 100
4.	SCOD	mg/L	200 ± 10
5.	pH	-	6.9
6.	Protein	-	0.043
7.	Carbohydrate	-	0.032

where $SCOD_p$ = SCOD concentration of the pretreated WAS(mg/L),$TCOD_i$ = Initial TCOD concentration of WAS, $SCOD_i$ = Initial SCOD concentration of WAS.

3. RESULTS AND DISCUSSION

3.1 Effect of operating parameters for Thermo-Fenton treatment process

The effectiveness of operational parameters such as contact time, temperature, Fe^{2+} and H_2O_2 dosage for Thermo-Fenton reaction was determined based on SCOD release and MLSS reduction. In fact, under acidic condition (pH=3), fenton reagent produces $^{\cdot}OH$ radicals by iron catalysed decomposition of H_2O_2. These radicals have an oxidizing potential and are capable of oxidizing a wide range of organics.

3.1 Effect of Thermo-Fenton process on sludge reduction

The MLSS reduction found using the standard method at the sampling intervals observed and plotted into the graph and the MLSS reduction efficiency calculated with respect to initial MLSS concentration. Iron plays a vital role for the Fenton oxidative degradation process. The levels of hydrogen peroxide is very important in the degradation of organic pollutant in WAS. It is a source of $^{\cdot}OH$ radical generation in the Fenton's reaction. The chart -1 depicts the MLSS reduction efficiency (%) on sludge at Fe^{2+}- 0.007 g/g SS & H_2O_2 – 7 µL from 50°C to 90°C. The maximum efficiency of 66.6% was achieved at 15 mins in 70°C.

3.2 Effect of Thermo-Fenton process on COD Solubilization

The efficiency of the sludge pre-treatment was measured in terms of the COD solubilization effectiveness. SCOD is an index for assessing disintegration competence [4]. Solubilization was increased during thermo-Fenton oxidation due to the components of EPS and cells which were acid hydrolyzed as well as partially oxidized by hydroxyl radicals. Thermal treatment on the thickened sludge was performed for five different temperatures and

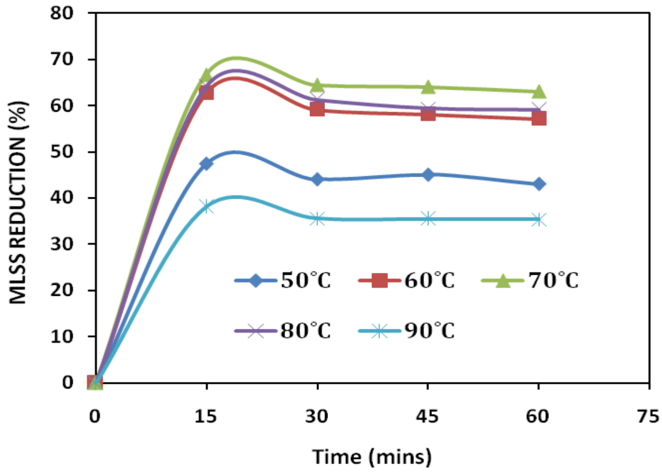

Chart -1: Optimization of temperature and time based on MLSS reduction

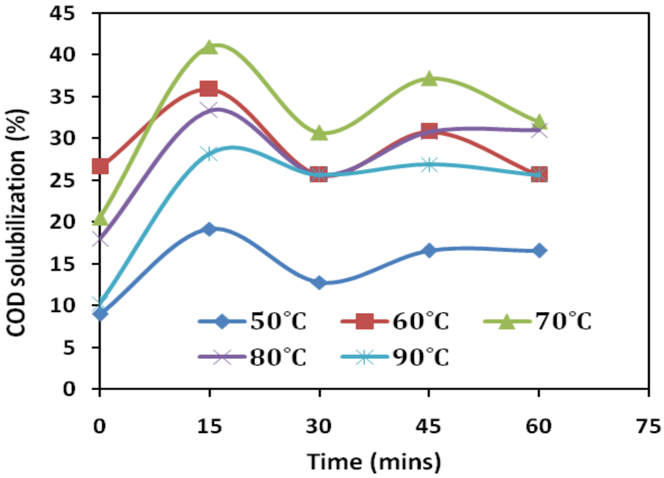

Chart -2: Optimization of temperature and time based on COD solubilization

treatment durations. In this study, it is clear that a thermal treatment effectively releases the studied components to the water phase. The chart -2 depicts the COD solubilization (%) on sludge at Fe^{2+}- 0.007 g/g SS & H_2O_2 – 7 µL from 50°C to 90°C. The maximum efficiency of 66.6% was achieved at 15 mins in 70°C.

3.3 Effect of Thermo-Fenton process on Protein and Carbohydrate

Disruption of flocs and removal of EPS improves the effectiveness of a disintegration process [5]. Therefore, to promote the competence of disintegration, sludge flocs were disrupted and EPS was removed by the Fenton process. Fenton reagent was added to the sludge to induce chemical oxidation and remove EPS surrounding the sludge biomass cells. This in turn eventually destabilized the biomass aggregation and disrupted the sludge matrix. The added Fe^{2+}

reacted with H_2O_2 and resulted in the generation of hydroxyl radicals which in turn could act upon the EPS layer and disrupt the sludge [6]. The protein & carbohydrate release at various temperature with the optimized fenton dosage are shown in the Chart-3 & Chart-4. The increment in protein release at phase I was due to the solubilization of EPS released from the bound phase to the aqueous phase. After 25 min of the fenton process, a steady decrement was evidently noticed up to 30 min. This could be attributable to the degradation of discharged organics from EPS layer through uninterrupted generation of OH radicals. These radicals began to break sludge cells (at 30 min) after complete degradation of released organic matter. Therefore, 15 min of disintegration time was observed to be optimal for sludge disintegration.

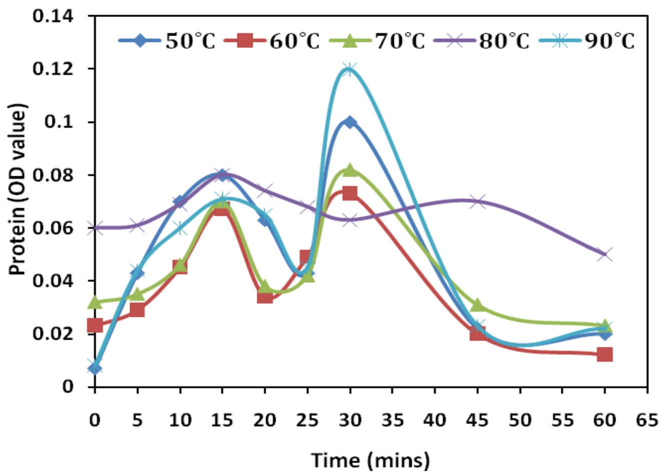

Chart -3: Effect of Thermo-Fenton treatment on protein release

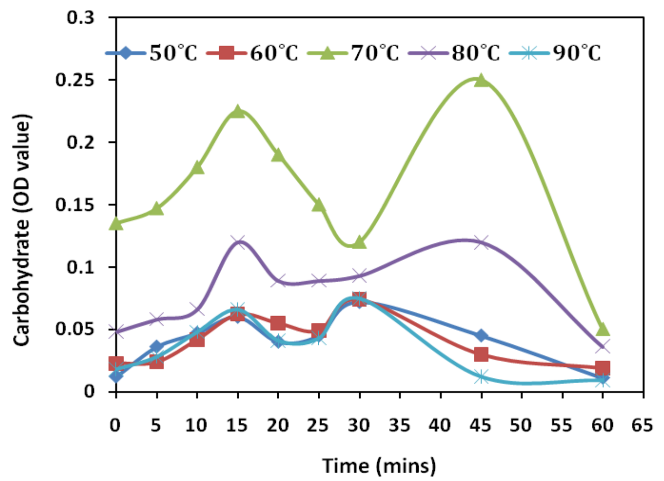

Chart -4: Effect of Thermo-Fenton treatment on carbohydrate release

4. CONCLUSION

The waste activated sludge has a complex nature and is mostly composed from organic substances and bacterial cells, which can be disintegrated to organic substances and oxidized to CO_2 and water using Fenton process. Due to many useful and unexpected interference reactions influencing disintegration efficiency in the complex nature of the WAS, this study was focused on determining the effects of main operational conditions (Fenton dosages, time & temperature), the kinetics based on the release of organic matters into the soluble phase of the WAS and the anaerobic biodegradability of the sludge under the optimum conditions. Experimental investigations revealed that Thermo-Fenton oxidation disrupted the sludge cells and caused the release of bound water and intracellular large molecular substances. As a result, the maximum sludge reduction efficiency and COD solubilization was found to be 66.6% and 41.02% respectively. It was seen that organic and inorganic compounds are efficiently solubilised during thermal pretreatment. The optimal conditions obtained from the response of moisture content are as follows: Fe^{2+} of 0.007 g/g SS, H_2O_2 of 7μL and contact time 15 min. And the optimal temperature for the pre-treatment process was found to be 70°C. Fenton oxidation degraded and damaged EPS caused the breakup of sludge matrix and microorganism cell lysis, promoting waste activated sludge dewatering characteristics. Due to its efficiency of sludge reduction even in lower dosage defines the effectiveness of proposed method. Finally in terms of industrial application, it seems obvious that pretreatments at high temperature are more advantageous than at lower temperature.

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