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Persuade of solar driven photo-Fenton process for the effective sludge reduction through chemical deflocculation

V. Amudha[a], J. Judes[b,*]

[a]*Department of Science and Humanities, Anna University Reginal Campus, Tirunelveli, Tamil Nadu, India, email: amudhajohnse@gmail.com*
[b]*Department of Science and Humanities, University VOC College of Engineering, Thoothukudi, Tamil Nadu, India, email: taj.judes@gmail.com*

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ABSTRACT

The present investigation deals with excess sludge reduction by the photo-Fenton reaction through sludge deflocculation using citric acid. Citric acid has been chosen as a cationic binding agent for deflocculation of sludge through the elimination of extra polymeric substances. Based on the preliminary experiments conducted in the laboratory, optimization of parameters such as, Fe dosage, H_2O_2 dosage and time were carried out. The optimized values have been observed as Fe dosage 0.004 g/g SS, H_2O_2 dosage 0.4 g/g SS and time 20 min. The addition of citric acid decreased the sludge pH to 5 that was advantageous in the photo-Fenton process to avoid the addition of acids and bases for the acidification and neutralization of the sludge samples at the beginning and end of the treatment procedure. It was evident from the study that the photo-Fenton process was profited by sludge deflocculation in the reduction of chemical oxygen demand, suspended solids and volatile suspended solids which was observed as 84%, 65% and 78%, respectively. Cost analysis divulged that sludge disposal cost can be reduced through deflocculation of sludge. From the overall result it is proved that the photo-Fenton process through deflocculation is the best suited for the reduction of excess sludge.

Keywords: Waste activated sludge; Deflocculation; Photo-Fenton process; Oxidation–reduction reaction; Organic reduction

1. Introduction

Advanced oxidation processes (AOPs) are concerned in the production of most reactive hydroxyl free radicals (•OH). Fenton reagent is one of the important and significant tools of AOPs. The researchers opted AOPs, especially in the sludge processing techniques explains these methods are imminent for the sludge reduction [1–3]. The Fenton reaction has prominent desirability over other AOPs such as ultraviolet, photo catalyst, sonolysis, photolysis, ozone-based process, electrochemical oxidation, owing to its distinctive value like short reaction time, cost effectiveness, easiness in running and controlling the process, non-toxicity and eco-friendliness [4]. The solids and biosolids which are generally exist in the state of liquid and semisolid are called as sludge that persist 0.25%–12% solids by weight according to the operation techniques. Sludge from the waste water treatment plants (WWTPs) contains organic materials, inorganic salts and pathogens. The disposal of excess sludge without prior treatment is highly harmful and contagious to the environment [5]. The most critical issue is treatment and disposal of sludge which are very much expensive for the industries and WWTPs [6]. Evidence were found for the treatment of various types of sludge using Fenton reagent [7–11]. Generally, waste activated sludge (WAS) surrounds extra polymeric substances

* Corresponding author.

(EPS) which acts as a shielding for sludge biomass in any adverse conditions [12]. Moreover, flocculation of sludge is achieved by EPS that could make all the extracellular enzymes are immobilized in flocs [13]. The major organic portion of EPS gives the integrity, strength and also determines the floc structure. So, it was concluded in a research work that disruption of EPS always increases the efficiency of sludge treatment processes [14]. In AOPs, the effectiveness is achieved in the treatment process with the greater requirement of energy and chemical [15]. Also in AOPs, operation cost is raised with the need of high energy photons that are generated by artificial light. On the other hand, photo-Fenton processes can be conducted using low energy photons which are available in the visible part of the electromagnetic spectrum. Many researchers have reported that the use of natural sunlight as radiating medium decreased the cost of photo catalytic processes [16–18]. The common reaction mechanism of Fenton process is decomposition of hydroxyl radical in the acidic medium with the presence of iron catalyst as shown in Eq. (1).

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

When the Fenton reaction is combined with ultraviolet or visible light, the production of hydroxyl radical occurred by Fe(III) and hydrogen peroxide as explained in Eq. (2). That is, Fe^{3+} is frequently reduced into Fe^{2+} during irradiation.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (2)$$

The Fenton reaction is influenced by the photo generated Fe^{2+} which acts as a catalyst for the reaction of produced hydroxyl radicals with targeted organic molecules.

However minimum studies were accounted on the photo-Fenton processes for the sludge pre-treatment and treatment, no information is available for the reduction of sludge by photo-Fenton process through chemical deflocculation. In this investigation, deflocculation of sludge was carried out using citric acid prior to photo-Fenton process in order to increase the mineralization of organic material through oxidation for the reduction of sludge. The assessment is made for the practical implementation of any treatment process through its economic possibility. So, this investigation is incorporated with practical opportunity of the method by providing data on economic assessment.

2. Materials and methods

2.1. Sludge collection

Sewage sludge from the return line of secondary clarifier of a local sewage treatment plant in Valiyathura, Trivandrum, Kerala, India, was collected in which 5 million L/d undertakes for treatment and stored at 4°C in the laboratory.

2.2. Sludge characterization

Initial characterization of sludge was carried out to obtain the parameter values such as pH, TCOD, SCOD, TS, TSS, volatile suspended solids (VSS) and MLSS/MLVSS. Accordingly, the observed values are pH 6.8, TCOD 8,000 ± 200 (mg/L), SCOD 100 ± 5(mg/L), TS 7,400 ± 500 (mg/L), TSS 5,000 ± 250 (mg/L), VSS 4,500 ± 100 (mg/L), MLSS/MLVSS 0.76.

2.3. Analytical methods

Standard methods were pursued to observe the values for chemical oxygen demand (COD), suspended solids (SS) and VSS [19]. pH determination was carried out using a pH meter (Deep vision, Digital pH meter). UV radiation in solar light is measured with solar power meter with resolution of 0.00–99.99 W/m^2. The values were observed in triplicates for all the conducted experiments. Based on our previous study [20] cost calculation was estimated to evaluate the economic viability of the treatment process. The energy concerned for stirring in deflocculation and photo-Fenton process was calculated based on Eq. (3) [21].

$$P = N_p \rho n D^3 \quad (3)$$

where P = power required, W; N_p = power number for impeller; ρ = density of sludge, kg/m^3; n = revolutions per second, r/s; D = diameter of impeller, m.

3. Experimental procedure

The first step of the experimental procedure was sludge deflocculation. 1,000 mL of conical flask was filled with 500 mL of the sludge sample. Citric acid of the value 0.06 g/g SS was added with sludge sample and incubated for 3 h for sludge deflocculation [22]. 5,000 mg/L value was set as initial mixed liquor suspended solids (MLSS) of the sludge sample. All the experiments were performed at room temperature. Initial pH value of the sludge sample was 6.8 and after deflocculation the value was observed as 5.

The second step of the experimental procedure was photo-Fenton oxidation. The experiments were carried out in 1 L capacity (20 cm × 12 cm × 4.2 cm) of borosilicate glass trays. After deflocculation 500 mL of sludge sample was taken in the trays and kept under solar radiation with the UV intensity 32 ± 3 W/m^2. Further, Fe^{2+} (0.001 to 0.009 g/g SS) and H_2O_2 (0.1 to 0.9 g/g SS) were added to the sludge sample and stirred well for the complete mixing of the reagents. The experiments were carried out with the pH value of 5 and the samples were collected in 5 min time interval for the determination of the response factors such as COD, SS and VSS.

4. Results and discussions

4.1. Effect of initial dosage of H_2O_2

The COD and SS reduction are enhanced with increasing the dosage of hydrogen peroxide till it reaches the optimum value. Maximum reduction is observed in the initial dosages due to the production of hydroxyl radical by photo-Fenton process. Based on the preliminary experiments conducted in the laboratory, the range of H_2O_2 dosage fixed as 0.1 to 0.9 g/g SS and reduction in COD and SS were observed in this fixed range. Fig. 1 depicts the optimum dosage of H_2O_2 was observed as 0.4 g/g SS. Higher dosages of H_2O_2 shows no considerable improvement in the sludge treatment procedure because of its scavenging effect. The following Eqs. (4) and (5) depict the scavenging effect of H_2O_2 when it is present excess in the reaction site.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (4)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow O_2 + H_2O \quad (5)$$

The reaction of OH radical and H_2O_2 and also the combinative reaction of two hydroxyl radicals may reduce the potential of COD and SS reduction [23]. Thus, the optimization of H_2O_2 plays a significant role in the treatment process.

4.2. Effect of initial dosage catalyst

The role of initial dosage of catalyst is important in the decomposition reaction of H_2O_2. Fe^{2+} acts as a catalyst in the Fenton reaction. The optimization of catalyst was carried out fixing the range of the catalyst as 0.001 to 0.009 g/g SS. From Fig. 2 it is evident that the optimum dosage of catalyst was found to be 0.004 g/g SS.

The light irradiation leads iron cycle connecting Fe^{2+} and Fe^{3+}. Solar based Fenton reaction leads a constant reduction of Fe^{3+} to Fe^{2+} that improves the constant production of hydroxyl radicals which targets organic materials for the oxidation reaction [24]. So, in the initial dosages of catalyst, the reduction range of COD and SS was observed greater in values. If excess catalyst is present in the reaction site leads the formation of chemical Fenton sludge and also decreases the neutralization of treated sludge [25].

The operational cost also raises the usage of excess catalyst. Another important effect of excess catalyst presence is scavenging effect of hydroxyl radicals which reduces the treatment efficiency of the process [26,27].

4.3. Effect of pH

Many studies in Fenton process refers as the optimum value of pH is 3 [2,7,28]. However, this extremely acidic state of reaction mixture in the Fenton process hinders the practical applicability by raising the cost and need chemicals for acidification as well as neutralization process before and after treatment. The pH value of the sludge changed from 6.8 to 5 through deflocculation using citric acid. It was revealed in our previous study that no significant changes in the treatment process at pH values 5 and 3 [20]. Considering this advantage, the present investigation also carried out at the pH value 5.

4.4. Chemical oxygen demand and suspended solids reduction

Deflocculation is attained by eliminating the divalent cations strongly holding the EPS with sludge employing the chemical citric acid as a cation binding agent. Total extractable EPS can be calculated by summing up loosely bound-EPS and tightly bound-EPS. The amount of extractable EPS was estimated to be 80 mg/L [20].

Experiments were conducted both in flocculated and deflocculated sludge samples to predict the values of COD and SS reduction for the optimum dosages of catalyst and H_2O_2 at pH value 5 with 45 min time duration of solar irradiation. An extreme increase of COD and SS reduction values were observed for the initial 10–20 min of time duration. From Fig. 3 the reduction percentage of COD and SS are measured as 84 and 65 respectively, for deflocculated and 45% and 30%, respectively, for the flocculated sludge samples.

Oxidation of microbes' cell wall and subsequent mineralization occurred by hydroxyl radical produced from Fenton reagent could be the reason for the higher reduction percentage of COD and SS at the initial stage of time duration. A noticeable fact is observed from the results of COD and SS reduction profile which is maximum reduction percentage is achieved in deflocculated sludge samples than

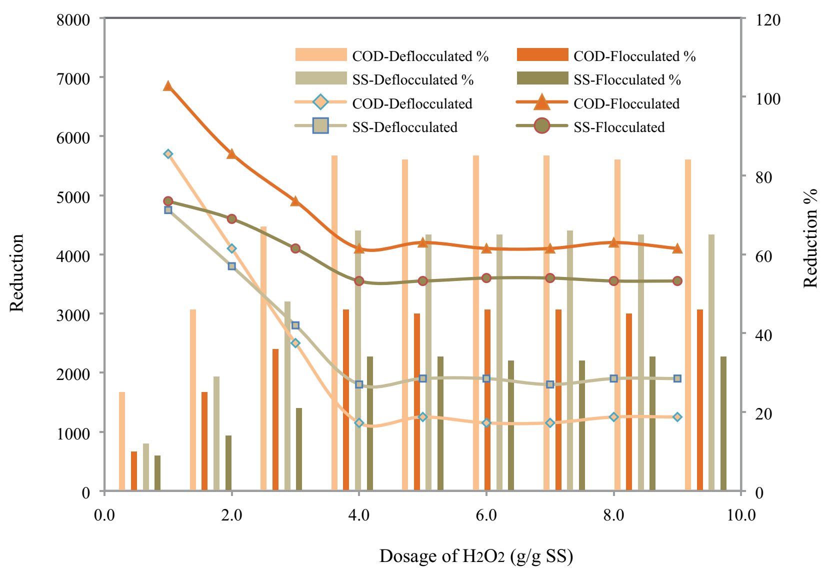

Fig. 1. Optimum COD and SS reduction as a function of H_2O_2 dosage.

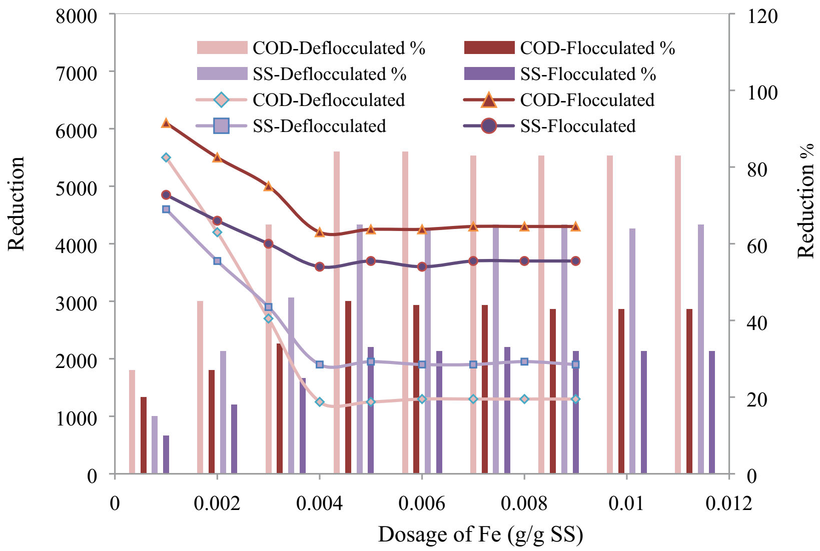

Fig. 2. Optimum COD and SS reduction as a function of Fe^{2+} dosage.

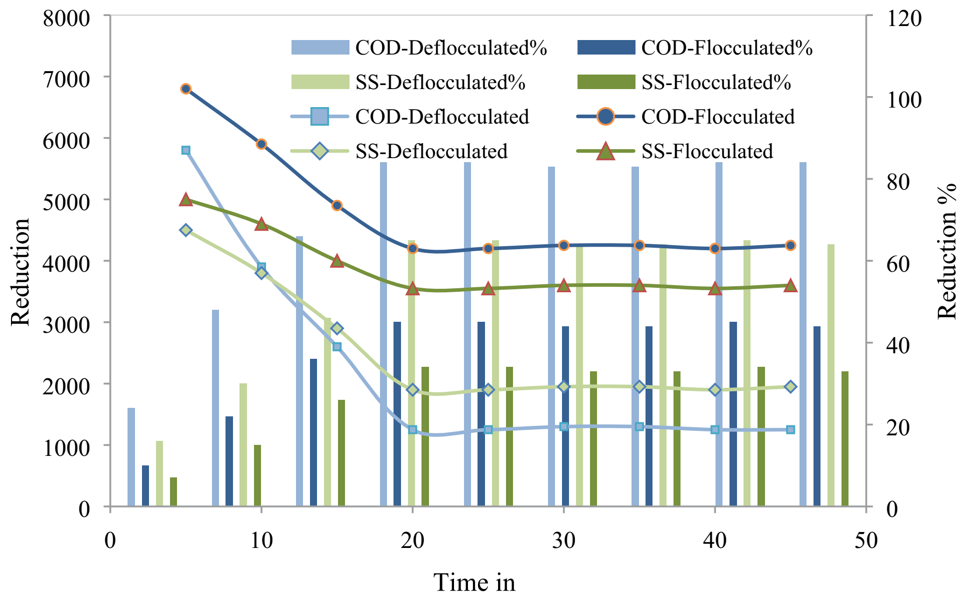

Fig. 3. Effect of photo-Fenton's reaction on COD and SS reduction.

the flocculated samples. The existence of EPS in the sludge formulates flocculants characteristic, which are responsible for the production of microbial colonies and protects microbial cells from harsh environment [29]. Elimination of the EPS from the sludge can influence the sludge biomass solubilization.

When deflocculated sludge undergoes Fenton reaction in the presence of solar irradiation that can influences the mineralization process greater comparing with flocculated sludge samples. The major advantage of Fenton process is short duration of reaction time. The present study depicts that the maximum reaction time observed for photo-Fenton process is 20 min which is observed less than the other treatment processes [30]. This attracts the process by reducing the capital cost investment for consequent scale up.

4.5. Volatile suspended solids reduction

Fig. 4 depicts the VSS reduction percentage observed both in flocculated and deflocculated sludge samples and the values are observed as 40% and 76%, respectively. In deflocculated sample higher reduction percentage is achieved than the flocculated sample. VSS study was carried out to enumerate the organic portion of sludge to predict the efficiency of the sludge management which depends on the organic matter reduction to a certain extent than inorganic matter [21].

Before start-up the treatment processes the MLVSS to MLSS was observed as 0.76. Following the treatment process the value was reduced into a greater extent that infers the degradation of organic matter through the treatment

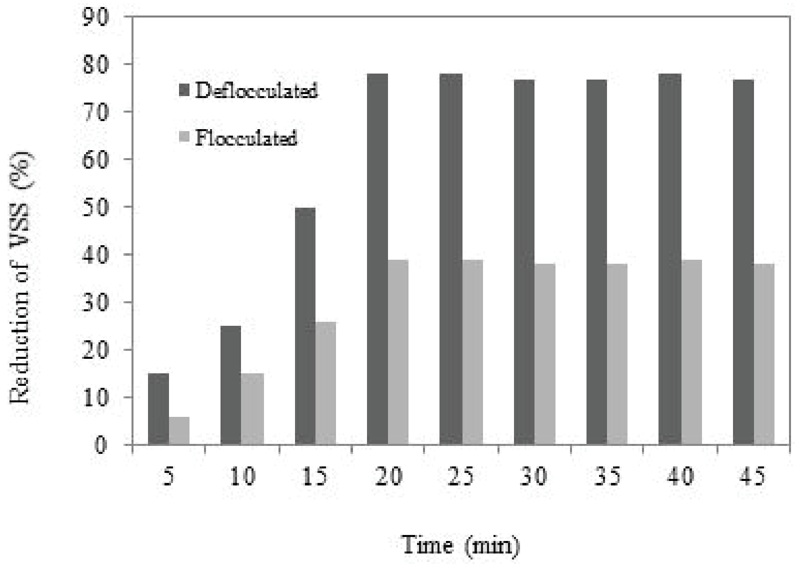

Fig. 4. Effect of photo-Fenton's reaction on VSS reduction.

process. This leads the subsequent sludge management process effortless [21].

4.6. Economic assessment

Practical implementation is a significant factor for any of the treatment process. The feasibility and field applicability of photo-Fenton process was also estimated through its economic capability. Generally, Fenton process focused in AOPs due to its easy operative methods. Sludge reduction processes such as chemical, thermal, and mechanical concentrates on disintegration only and it requires additional facility for degradation, further increases the capital cost. In the present study, disintegration and degradation carried out concurrently this reduces capital cost [31]. So, the economic analysis made hereby based on its operative method and cost related factors [32]. By balancing the input and out energy for the treatment process a net energy production is calculated [33,34]. In the present study during the treatment process there is no energy production is observed since the organics present in the sludge get neutralised. So, only input energy is calculated for the treatment process. The energy consumption occurred in every stage of the process tabulated in Table 1.

Accordingly, the energy consumed for the deflocculation, photo-Fenton and sludge dewatering process was predicted as 7.23, 2.41 and 77.5 kWh, respectively. Cost analysis carried out considering the factors such as cost for energy utilization and cost for chemical purchase and cost calculation in view of final disposal of sludge. Table 2 depicts the elaborate analysis of cost required for the treatment process.

The net cost was calculated in terms of USD per ton which was observed as –6.0 USD/ton and –180.6 USD/ton for deflocculated sludge and flocculated sludge, respectively. Economic analysis concludes that photo-Fenton process through deflocculation is an profitable method for the excess sludge disposal.

5. Conclusions

The most effective cationic binding agent, citric acid was used for the disruption of sludge flocs. The laboratory scale studies were carried out to predict the feasibility of photo-Fenton process for the reduction of excess sludge. Process efficiency was achieved through the assessments of the effects of parameters such as initial concentration of Fenton reagent, time and pH. On comparing the outcome of reduction percentage of COD and SS for the flocculated and deflocculated sludge the benefit of deflocculation was predicted. The degradation of organics was observed through VSS summary. Economic viability was calculated through the analysis of energy consumption and disposal cost.

Table 1
Energy consumption (kWh) per ton SS of sludge

S. No.	Energy applied	Flocculated	Deflocculated	Control
1	EPS removal	–	7.23	–
2	Photo-Fenton	2.41	2.41	–
3	Sludge dewatering	77.5	77.5	77.5
	Total	79.91	87.14	77.5

Table 2
Cost analysis (per ton SS of sludge)

S. No.	Content	Flocculated	Deflocculated	Control	Unit
1	Energy cost (Energy × 0.23 USD/kWh)	18.4	20.0	17.8	USD
2	Consumable cost				
	Citric acid	–	8.16		
	H_2O_2	50.4	50.4		USD
	Fe^{2+}	0.055	0.055		
3	Consumable cost (2*a* + 2*b* + 2*c*)	50.4	58.6	–	USD
4	Decreased in SS to be disposed	300	650	–	kg
5	SS to be disposed	700	350	1,000	kg
6	Sludge disposal cost (S. No. 5 × 0.28 USD/kg SS)	196	98	280	USD
7	Reduced sludge disposal cost (S. No. 4 × 0.28 USD/kg SS)	84	182	–	USD
8	Net cost (8 – (2 + 4 + 7))	–180.8	–6.0	–297.8	USD

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