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Efficiency of zero valent iron in the modified Fenton process for the reduction of excess sludge and the key role of citric acid through deflocculation

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ABSTRACT

The study aimed for the excess sludge reduction by modified Fenton process (MFP) using zero valent iron (ZVI, Fe^0) as a catalyst under the influence of sludge deflocculation. Citric acid was employed as a cationic binding agent to deflocculate the sludge by eliminating extracellular polymeric substances to improve the efficiency of the treatment process. The optimization of operational parameters such as pH, initial dosages of Fe^0 and H_2O_2 and time were performed elaborately for the MFP by response surface methodology. The optimum conditions have been found as Fe^0 dosage of 0.006 g/g suspended solids (SS), H_2O_2 dosage of 0.5 g/g SS and pH value of 3.5 with 50 min oxidation time period. The benefit of deflocculation was evident from the study as deflocculated sludge undergoing MFP produced higher reduction percentage of chemical oxygen demand, SS and volatile suspended solids than the control. Kinetic analysis was carried out under optimal conditions which prove that the rate was four times higher in the deflocculated sludge. Cost analysis revealed that ZVI mediated Fenton process through deflocculation reduced the sludge disposal cost. The unsolved ZVI can be separated easily from the reaction mixture using magnet to avoid iron contamination in the treated sludge at the end of the process. It is evident from the overall result of the study that ZVI can be successfully replaced for ferrous salt as a catalyst to carry out Fenton reaction. Subsequently, deflocculation improves the process efficiency.

Keywords: Activated sludge; Deflocculation; Response surface methodology; Zero valent iron; Modified Fenton process; Suspended solids reduction

1. Introduction

The sludge management is one of the most complicated and expensive process in the wastewater treatment plants (WWTPs). The treatment and disposal cost of excess sludge accounts for 40% of the capital cost and 50% of the operating cost of the WWTP [1]. Therefore, sludge treatment is mandatory before its disposal. Generally, biological treatment processes have been taken greater consideration due to energy recovery from waste stabilization [2,3]. On the other hand, inadequate hydrolysis of particulate organics present in the sludge bounds the competence of biological treatment processes.

The method based on advanced oxidation processes (AOPs) becomes different approach used with great success at WWTPs for sludge management [4,5]. In AOPs hydroxyl radical is the key oxidant [6]. The Fenton process is considered the most promising for the remediation of highly polluted wastewaters and sludges between the various AOPs [7]. The oxidative system of the Fenton process is more striking due to the need of inexpensive reagents and non-complicated instrumentation for the pollutant destruction [8]. One of the most identified Fenton process is conventional Fenton process (CFP), for the treatment of highly complicated pollutant like biorefactory [9]. The oxidation of organic compounds (RH) by CFP is carried out as per Eqs. (1)–(4) [10,11].

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

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

$$RH + {}^{\bullet}OH \rightarrow H_2O + R^{\bullet} \quad (3)$$

$$R^{o} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \quad (4)$$

However, the production of $Fe(OH)_3$ precipitate is considered as the major drawback of CFP [12]. To overcome this problem, the application of substitute iron sources as organically modified catalyst has been studied extensively which is called as modified Fenton process (MFP) [13,14].

The fourth most abundant element on the earth is iron with the advantages of non-toxic and safe. Whereas, the oxidant hydrogen peroxide possess various benefits like easy handling, environmentally friendly and reasonable price than the other oxidants [15]. In the MFP zero valent iron (ZVI, Fe^0) in the form of powder can also be employed as the catalyst. The first step of the MFP is dissolution of ZVI from the metallic surface under strongly acidic conditions which gives the product as per Eq. (5). Further, the solved iron rapidly reacts with H_2O_2, which follows the reaction steps of CFP.

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \quad (5)$$

The transformation of Fe^{3+} into Fe^{2+} is carried out on the metallic surface of the ZVI, follows Eq. (6), and increases the oxidation potential of the process. This results the less production of chemical Fenton sludge which is the most important advantage of this MFP. Finally, the unsolved ZVI can be easily removed by magnetic separation from the sludge [14].

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad (6)$$

Extracellular polymeric substances (EPSs) are organic polymers which present in the cell surface responsible for flocculation characteristics of the sludge [16]. The cations and the complex molecules present in the EPS plays an important role in flocculation [17]. Biomass solubilization can be improved by the elimination of EPS. Many methods have been reported for the removal of EPS from the sludge matrix to improve the efficiency of the treatment process. Citric acid is one of the most effective cation binding agent that bind with the cations of EPS for its extraction from the cell surface [18]. In the present study, citric acid is utilized for deflocculation through the removal of EPS. Further, MFP was carried out using ZVI instead of ferrous salt which is conventionally used in Fenton reagent. The usage of ZVI in the Fenton process for sludge reduction through deflocculation has not been renowned in the literature so far. The main objectives were (1) to optimize the modified Fenton dosage and reaction time for the effective treatment of the sludge, (2) to investigate the effect of deflocculation on the efficiency of MFP, (3) to determine the rate of the reaction through kinetic investigations and (4) to evaluate the proficiency of deflocculated and ZVI mediated Fenton treatment through cost assessment.

2. Methods and materials

2.1. Sludge sampling

Municipal waste activated sludge was collected from the secondary clarifier of a sewage treatment plant at Trivandrum, Kerala. The collected sample was stored at 4°C for 24 h in the laboratory for further studies. The raw sludge had initial characteristics of pH 6.25, total chemical oxygen demand (COD) 8,000 mg/L, soluble COD 100 mg/L, total solids (TS) 7,300 mg/L, suspended solids (SS) 5,000 mg/L, dissolved solids 2,300 mg/L and volatile suspended solids (VSS) 4,400 mg/L.

2.2. Optimization of modified Fenton oxidation conditions by RSM

The optimization of modified Fenton oxidation conditions was carried out by response surface methodology (RSM). A central composite design (CCD) made with Design-Expert software was utilized to examine the simultaneous effect of four independent variables: H_2O_2 dosage, ZVI dosage, pH and time. COD and SS reduction of the sludge sample was analyzed to optimize the H_2O_2 dosage, ZVI dosage, pH and time for Fenton's oxidation. As per ground work carried out, the range of H_2O_2 dosage, ZVI dosage, pH and time was fixed as 0.1–0.9 g/g SS, 0.001–0.01 g/g SS, 2–7 and 0–90 min, respectively. From the RSM results 30 experiments were set with the target responses COD and SS (mg/L) of sludge.

2.3. Experimental procedure

2.3.1. Modified Fenton oxidation through sludge deflocculation

ZVI was used as a catalyst iron source for MFP. Initial mixed liquor suspended solids (MLSS) of the sludge sample was fixed as 5,000 mg/L. Experiments were conducted at room temperature.

The 100 mL of the sludge sample was poured into each 250 mL conical flask with 0.06 g/g SS citric acid and incubated for 3 h for deflocculation [19]. The pH value of the sample was observed as 5 after deflocculation. Further, the pH value of the reaction was adjusted to 3.5 by adding H_2SO_4. Afterwards, ZVI (0.001–0.01 g/g SS) and H_2O_2 (0.1–0.9 g/g SS) were added in suitable dosages to the reaction mixture and stirred at 160 rpm. In 10-min intervals, samples were collected and analyzed for COD, SS and VSS reduction.

2.4. Analytical methods

COD, SS and VSS were calculated according to the standard measurement methods [20]. pH of the reaction mixture was determined by using a pH meter. All the experiments were conducted in triplicate.

2.5. Energetic analysis and cost calculation

Based on a pilot scale treatment process the cost assessment of treatment methods was carried out. The experimental values obtained from the pilot scale study were taken into account for the calculation of energy studies and economic analysis to evaluate the efficiency of the treatment process. The cost calculation was estimated for 1 ton of sludge based on our previous study [19]. The energy applied for stirring in deflocculation and modified Fenton treatment was calculated based on Eq. (7) [21]:

$$P = N_p \rho n D^3 \tag{7}$$

where P is the power required, W; N_p is the power number for impeller; ρ is the density of sludge, kg/m^3; n is the revolutions per second, rps and D is the diameter of impeller, m.

3. Results and discussion

3.1. Effect of EPS removal on MFP

EPS is a complex organic molecule that congregates on the cell surface of the sludge biomass and affords stability to the biomass [22]. The addition of cation-binding agents removes cations that clutch EPS in the sludge matrix. Consequently, the floc network was destroyed, and it paved way for enhanced solubilization of sludge microbes [23]. Citric acid is one of the most successful cation binding agent which binds with Ca^{2+} and Mg^{2+} ions of sludge matrix and disturb floc structure. For this study, an optimized citric acid dosage of 0.06 g/g SS was used to deflocculate the sludge and details of the optimization studies were mentioned in our previous study [19]. In order to examine, the influence of EPS removal on the MFP, the experiments were carried out in the flocculated and deflocculated sludge samples. The predictable effect of the sludge treatment was focused on COD and SS reduction to evaluate the efficiency of MFP.

3.2. Optimization of modified Fenton reagent dosage, pH and time by RSM

The optimization of parameters for MFP was carried out by implementing the CCD. The process variables such as, H_2O_2 dosage, ZVI dosage, pH and time influences the efficiency of the MFP [24]. COD and SS reduction was considered as a response factors to optimize process variables for the efficient MFP.

The coefficient of the model equation applied to predict the optimum COD and SS reduction was analyzed through regression analysis. The model fit through regression analysis was evaluated by determination coefficient R^2. Fisher's test (F value) and its interactive probability (p) value were analyzed to check the model significance. A strong correlation between the predicted and observed values was evident from the results of ANOVA analysis. The accuracy of the generated model was assessed through determination coefficient (R^2). The calculated R^2 values were seems to be 0.9975 and 0.9963, respectively. The adjusted and predicted R^2 values were observed as 0.9952 and 0.9929, and 0.9869 and 0.9839 for COD and SS reduction, respectively. The difference between the predicted and adjusted R^2 value was less than 0.2 which showed that the predicted R^2 was in reasonable agreement with the adjusted R^2.

The significance of each process variables are shown in Tables 1 and 2. From Tables 1 and 2, the calculated F values of the model were seems to be 427.04 and 292.04 with a very less probability (p) value of about <0.0001. This shows a greater significant impact of MFP. Similarly, the significance of the linear, quadratic and interactive terms was also evaluated and summarized in Tables 1 and 2. Based on the p value, all the process variables and its quadratic terms were most significant whereas the interactive terms were less significant in affecting the COD and SS reduction. The F values of the

Table 1
Analysis of variance for a quadratic response surface model with respect to COD reduction

Source	Sum of squares	df	Mean square	F value	p Value prob > F	
Model	1.016E+008	14	7.257E+006	427.04	<0.0001	Significant
A – H_2O_2	9.589E+006	1	9.589E+006	564.24	<0.0001	
B – Fe^{2+}	4.638E+006	1	4.638E+006	272.90	<0.0001	
C – time	4.111E+007	1	4.111E+007	2,418.98	<0.0001	
D – pH	1,504.17	1	1,504.17	0.089	0.7702	
AB	3.691E+005	1	3.691E+005	21.72	0.0003	
AC	3.335E+005	1	3.335E+005	19.63	0.0005	
AD	8.055E+005	1	8.055E+005	47.40	<0.0001	
BC	7.877E+005	1	7.877E+005	46.35	<0.0001	
BD	4.523E+005	1	4.523E+005	26.61	0.0001	
CD	3.221E+005	1	3.221E+005	18.95	0.0006	
A^2	1.771E+007	1	1.771E+007	1,042.41	<0.0001	
B^2	1.844E+007	1	1.844E+007	1,085.00	<0.0001	
C^2	1.481E+007	1	1.481E+007	871.69	<0.0001	
D^2	1.024E+007	1	1.024E+007	602.84	<0.0001	
Residual	2.549E+005	15	16,993.89	–	–	
Lack of fit	2.246E+005	10	22,457.50	3.70	0.0807	Not significant
Pure error	30,333.33	5	6,066.67	–	–	
Corr. total	1.019E+008	29	–	–	–	

Table 2
Analysis of variance for a quadratic response surface model with respect to SS reduction

Source	Sum of squares	df	Mean square	*F* value	*p* value prob > *F*	
Model	2.359E+007	14	1.685E+006	292.04	<0.0001	Significant
A – H_2O_2	2.781E+006	1	2.781E+006	482.06	<0.0001	
B – Fe^{2+}	5.251E+005	1	5.251E+005	91.01	<0.0001	
C – time	8.604E+006	1	8.604E+006	1,491.31	<0.0001	
D – pH	204.17	1	204.17	0.035	0.8533	
AB	6,006.25	1	6,006.25	1.04	0.3238	
AC	3.630E+005	1	3.630E+005	62.92	<0.0001	
AD	82,656.25	1	82,656.25	14.33	0.0018	
BC	6,006.25	1	6,006.25	1.04	0.3238	
BD	1.243E+005	1	1.243E+005	21.54	0.0003	
CD	5.293E+005	1	5.293E+005	91.73	<0.0001	
A^2	3.107E+006	1	3.107E+006	538.52	<0.0001	
B^2	4.099E+006	1	4.099E+006	710.41	<0.0001	
C^2	3.761E+006	1	3.761E+006	651.94	<0.0001	
D^2	4.099E+006	1	4.099E+006	710.41	<0.0001	
Residual	86,541.67	15	5,769.44	–	–	
Lack of fit	59,458.33	10	5,945.83	1.10	0.4888	Not significant
Pure error	27,083.33	5	5,416.67	–	–	
Corr. total	2.368E+007	29	–	–	–	

lack of fit were noted as 3.70 and 1.10 with the *p* values of about 0.0807 and 0.4888 for COD and SS reduction, respectively. From the above results, the lack of fit was found to be not significant. Hence, it can be concluded that the model is more significant. The influence of the independent factors on the dependent parameters is demonstrated in the response surface plots (Figs. 1 and 2). The combined influence of ZVI dosage, H_2O_2 dosage, pH and contact time on COD and SS reduction was evaluated from the figures.

The quadratic equation and its coefficients are precised as follows:

$$\begin{aligned}\text{COD} = {} & +9{,}368.15104 - 7{,}282.29167 \times H_2O_2 - 6.60911\text{E}{+}005 \\ & \times Fe^{2+} - 62.27083 \times \text{time} - 304.37500 \times \text{pH} \\ & + 9{,}4921.87500 \times H_2O_2 \times Fe^{2+} - 9.02344 \times H_2O_2 \times \text{time} \\ & + 160.26786 \times H_2O_2 \times \text{pH} - 1{,}386.71875 \times Fe^{2+} \times \text{time} \\ & - 12{,}008.92857 \times Fe^{2+} \times \text{pH} - 1.01339 \times \text{time} \times \text{pH} \\ & + 5{,}022.78646 \times H_2O_2{}^2 + 5.12435\text{E}{+}007 \times (Fe^{2+})^2 \\ & + 0.45931 \times \text{time}^2 + 49.88946 \times \text{pH}^2\end{aligned}$$

$$\begin{aligned}\text{SS} = {} & 6{,}160.57292 - 2{,}736.19792 \times H_2O_2 - 3.48932\text{E}{+}005 \times Fe^{2+} \\ & - 28.13281 \times \text{time} - 220.20833 \times \text{pH} + 12{,}109.37500 \\ & \times H_2O_2 \times Fe^{2+} - 9.41406 \times H_2O_2 \times \text{time} + 51.33929 \times H_2O_2 \\ & \times \text{pH} - 121.09375 \times Fe^{2+} \times \text{time} + 6{,}294.64286 \times Fe^{2+} \times \text{pH} \\ & - 1.29911 \times \text{time} \times \text{pH} + 2{,}103.51563 \times H_2O_2{}^2 \\ & + 2.41602\text{E}{+}007 \times (Fe^{2+})^2 + 0.23145 \times \text{time}^2 + 31.55612 \times \text{pH}^2\end{aligned}$$

It is well known that, pH plays a significant role in the Fenton and MFP during the oxidation of pollutants by scheming the catalytic activity, stability of H_2O_2 and activity of iron species. The oxidation potential in various pH values directly affects the concentration of the catalyst and the amount of OH radicals produced by Fenton reagents.

At highly acidic conditions, the formation of complex species $[Fe(H_2O)_6]^{2+}$ is observed which slows down the reaction and reacts more slowly with peroxide compared with that of $[Fe(OH)(H_2O)_5]^{2+}$. Consequently, the stable oxonium ion $[H_3O_2]^+$ is formed due to the salvation of peroxide in the presence of high concentration of H^+ ions. The peroxide is converted into electrophilic with the enhancement of its stability and substantially by the formed oxonium ion, which decreases the reactivity with Fe^{2+} ion [25,26]. The regeneration process of Fe^{2+} is hindered because of the reaction of Fe^{3+} with H_2O_2 and also stabilization of H_2O_2 into $H_3O_2^+$ is occurred as per Eq. (8) [27]. Furthermore, the scavenging effect of OH radical is taken place due to the reaction of H^+ ions with OH radicals which is given in Eq. (9) [28]. As a result, the oxidation efficiency of the overall process decreases because of the production of less OH radicals at high acidic pH values [9].

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{8}$$

$$^{\bullet}OH + H^+ + e^- \rightarrow H_2O \tag{9}$$

At low acidic values, ferryl ions which come under weaker oxidants were formed, that are more prominent than OH radicals. The very slow reaction of ferrous and ferric oxyhydroxide compounds with H_2O_2 results the reduction of the amount of free Fe^{2+} [29]. The following reasons also included for the inefficient degradation process at higher pH values: the lower oxidation potential of hydroxyl radicals, decomposition of H_2O_2 and deactivation of catalyst due to the formation of ferric hydroxide complexes [30]. All these facts accounts for the decrement in process efficiency. Therefore, pH 3.5 was taken as optimum pH value for the treatment process which resulted in the highest COD and SS reduction.

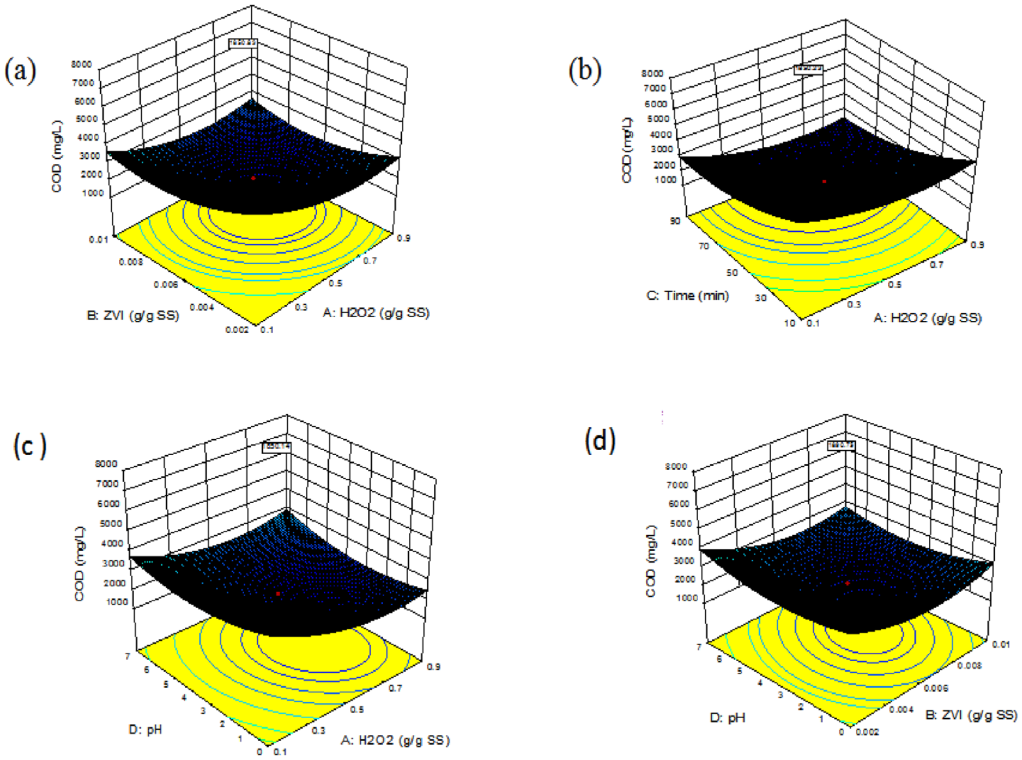

Fig. 1. Response surface plot showing optimum COD reduction: (a) as a function of ZVI and H_2O_2 dosage, (b) as a function of time and H_2O_2 dosage, (c) as a function of pH and H_2O_2 and (d) as a function of pH and ZVI dosage.

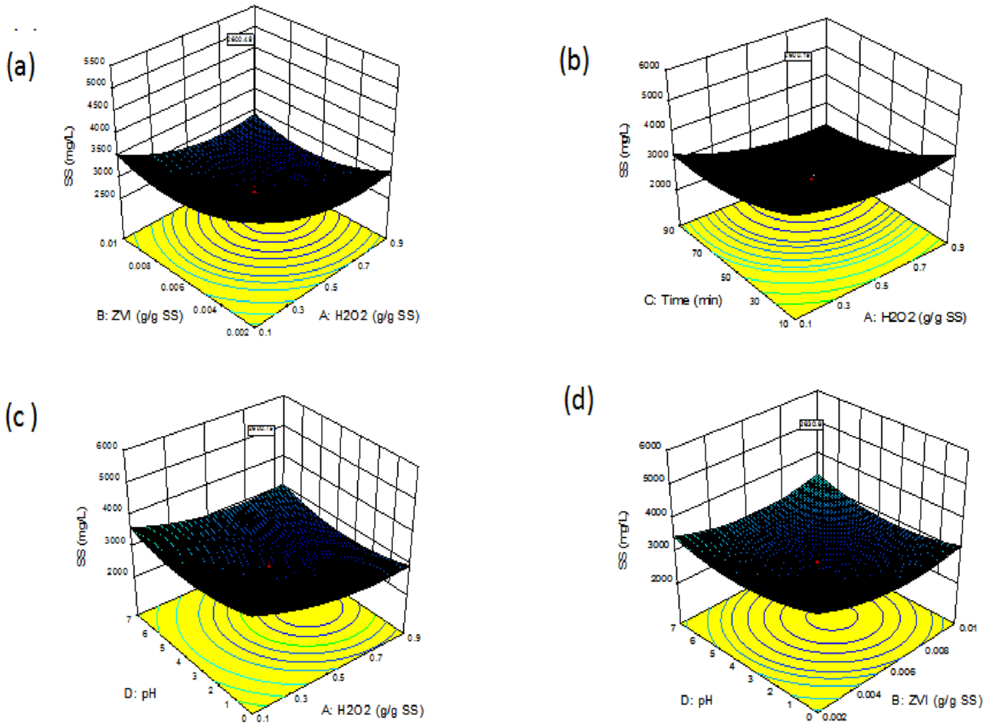

Fig. 2. Response surface plot showing optimum SS reduction: (a) as a function of ZVI and H_2O_2 dosage, (b) as a function of time and H_2O_2 dosage, (c) as a function of pH and H_2O_2 and (d) as a function of pH and ZVI dosage.

From the RSM, the optimum dosage of H_2O_2 was reported to be 0.5 g/g SS. If the dosage is increased more than 0.5 g/g SS, there is no significant progress in the treatment process. The scavenging effect of excess H_2O_2 may affect the treatment process above the optimized value which could be articulated with Eqs. (10) and (11) [31]. The decrease in COD and SS reduction values may be the reaction between OH radical and H_2O_2 and combination of two OH radical to produce H_2O_2 [25]. Moreover, the formed OOH radical is less reactive than OH radical reduces the rate of the reaction significantly. Many researchers reported in the same way in the degradation of pollutants by Fenton and MFP [32].

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (10)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow O_2 + H_2O \qquad (11)$$

Hence, 0.5 g/g SS of H_2O_2 was recorded as the optimum dosage.

In the Fenton processes, production of OH radicals through the decomposition of H_2O_2 plays a major role in the presence of Fe^{2+} as a catalyst. If excess of catalyst present in the reaction mixture results the formation of chemical Fenton sludge which affects the reusage of treated sludge and also increases the cost of the treatment process. So, it is necessary to optimize the dosage of iron catalyst [9]. 0.006 g/g SS of ZVI is recorded as optimized value for ZVI dosage. However, further increase in the iron dosages shows negligible improvement in the treatment process. This is may be the rapid transformation of Fe^{2+} to Fe^{3+} and the availability of less quantity of Fe^{2+} to proceed the OH radical production. Scavenging effect of OH radical also occurs at the higher dosages of catalyst that decreases the degradation processes. Thus, the optimal dosage of ZVI was observed to be 0.006 g/g SS.

Highest desirability of 100% was reached at 0.5g/g SS of H_2O_2 dosage, 0.006 g/g SS of Fe^{2+} dosage with the pH value of 3.5 for the contact time of 50 min. The optimal SS and COD reduction of about 2,800 and 1,850 mg/L was achieved at optimized pH, ZVI dosage, H_2O_2 dosage and contact time. The results of response surface plots implies that the combined effect of ZVI with H_2O_2, pH with H_2O_2, pH with ZVI have significant influence on MFP whereas the combined effect of interactive terms such as time with H_2O_2, time with ZVI and time with pH have less significant influence on MFP. The actual process optimization was done using a point optimization tool of design expert software 8 version. The central point corresponds to 0.5 g/g SS of H_2O_2 dosage, 0.006 g/g SS of Fe^{2+} dosage, pH value of 3.5 for the 50 min time duration.

3.3. Assessment on total COD reduction

In this section detailed experiments were carried out at the RSM predicted optimized condition to assess the efficiency of MFP with interest focused on sludge reduction performance assessment parameters such as COD and solids reduction. Fig. 3 depicts the reduction percentage of COD in both control and deflocculated sample by MFP. The values were observed to be 76% and 38% for deflocculated and control, respectively. The results were consistent with Amudha et al. [19] for Fenton reagent (H_2O_2 dosage of 0.5 g/g SS and Fe^{2+} dosage of 0.005 g/g SS) to be 72% and 34% for deflocculated and control, respectively. Linear fit analysis was carried out and presented in Fig. 3. The existence of two linear phases in the study period is revealed from the linear fit analysis. First linear phase is extended up to 50 min and resulted in the rate constant (k) value as 49.18 and 127 min^{-1} for the control and deflocculated, respectively. R^2 value lies between 0.92 and 0.99 which shows the goodness of fit. Second linear phase starts from 51 min and was carried out up to 51 min. The k value was observed to be 8 and 1 min^{-1} for the control and deflocculated, respectively, which shows insignificant changes in the reduction of COD. When comparing the results of deflocculated and control sludge it is clear that the reaction process enhanced by the deflocculation of the sludge. This is due to the elimination of EPS from the sludge matrix enhanced the reaction rate of the OH radicals with microbes for the cell wall decomposition and subsequent mineralization process.

3.4. Assessment on total VSS reduction

Figs. 4 and 5 illustrate the VSS reduction and reduction percentage achieved by the treatment process. From Fig. 5,

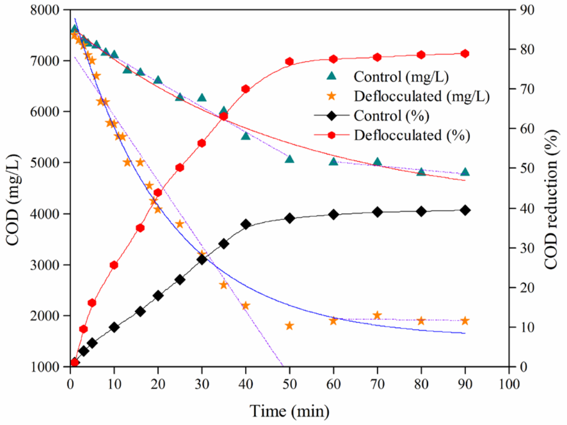

Fig. 3. Kinetic analysis of COD reduction using linear curve fitting and COD reduction percentage during modified Fenton process.

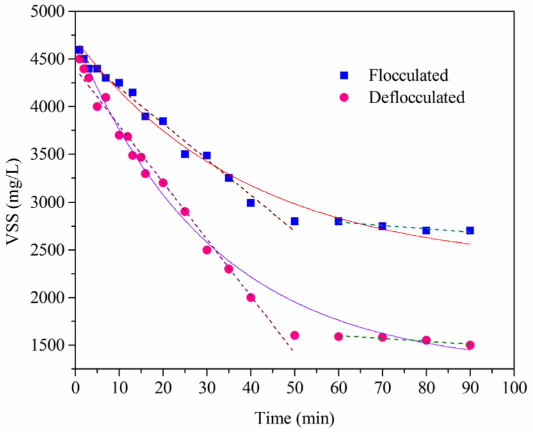

Fig. 4. Kinetic analysis of VSS reduction during modified Fenton process using linear curve fitting.

the value of VSS reduction percentage was found to be 39% and 65% of reduction for the control and deflocculated sludge, respectively. The linear fit assessment on total VSS reduction was carried out to analyze the effect of deflocculation in the MFP. There are two linear phases related with the present study which is shown in Fig 4. Phase I starts from 0 min and extend up to 50 min, resulting R^2 value was in the range of 0.92–0.99 which shows the goodness of fit. Rate constant (*k*) value was observed to be 37.5 and 59.6 min^{-1} for the control and deflocculated, respectively. Phase II starts from 51 min and extend up to 90 min. The *k* value for phase II was observed to be 3.5 and 3 min^{-1} for the control and deflocculated sludge, respectively, and it indicate insignificant changes in the reduction of VSS. From the results it is revealed that deflocculation enhances VSS reduction. Mineralization of organics by MFP also analyzed in terms of MLVSS and MLSS ratio and depicted in Fig 5. Initially, the value was found to be 0.8. Then, it fell down to a value of 0.2 after the treatment process time indicating reduction of organics and accumulation of inorganic. It indirectly helps to ease sludge management practices as it is well known that less organics in sludge favours sludge management practices [21].

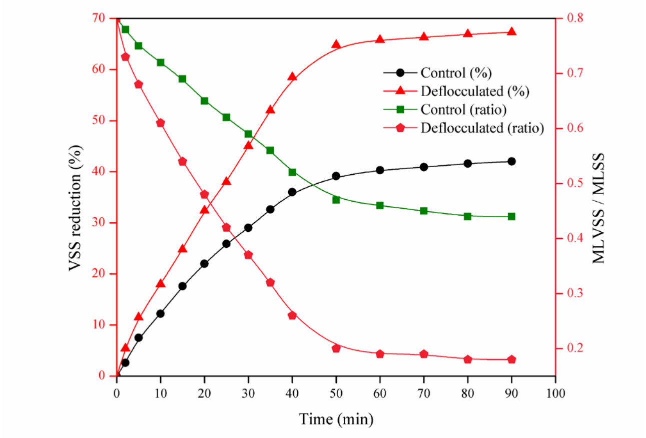

Fig. 5. Effect of modified Fenton process on VSS reduction percentage and MLVSS to MLSS ratio.

3.5. Economic analysis

Economic analysis decides the practical implementation of any treatment process. Low capital cost and easy handling are the two important advantages associated with MFP. In case of other sludge reduction process (thermal, chemical, mechanical) the focus is on disintegration only and it demands creation of additional facility for its degradation, thus increases the capital investment [33]. In MFP sludge disintegration and degradation takes place simultaneously and it reduces capital and operational cost. The cost estimation of the present study is detailed in Fig. 6. Energy cost and consumable cost are the main parameters associated with operational cost and were taken into account for the calculation. Energy required for agitation [21], for dewatering [34] and consumable cost was calculated and is presented in Fig. 6. The total energy cost was calculated to be 18.4 and 20 in US$, respectively, for control and deflocculated. While comparing

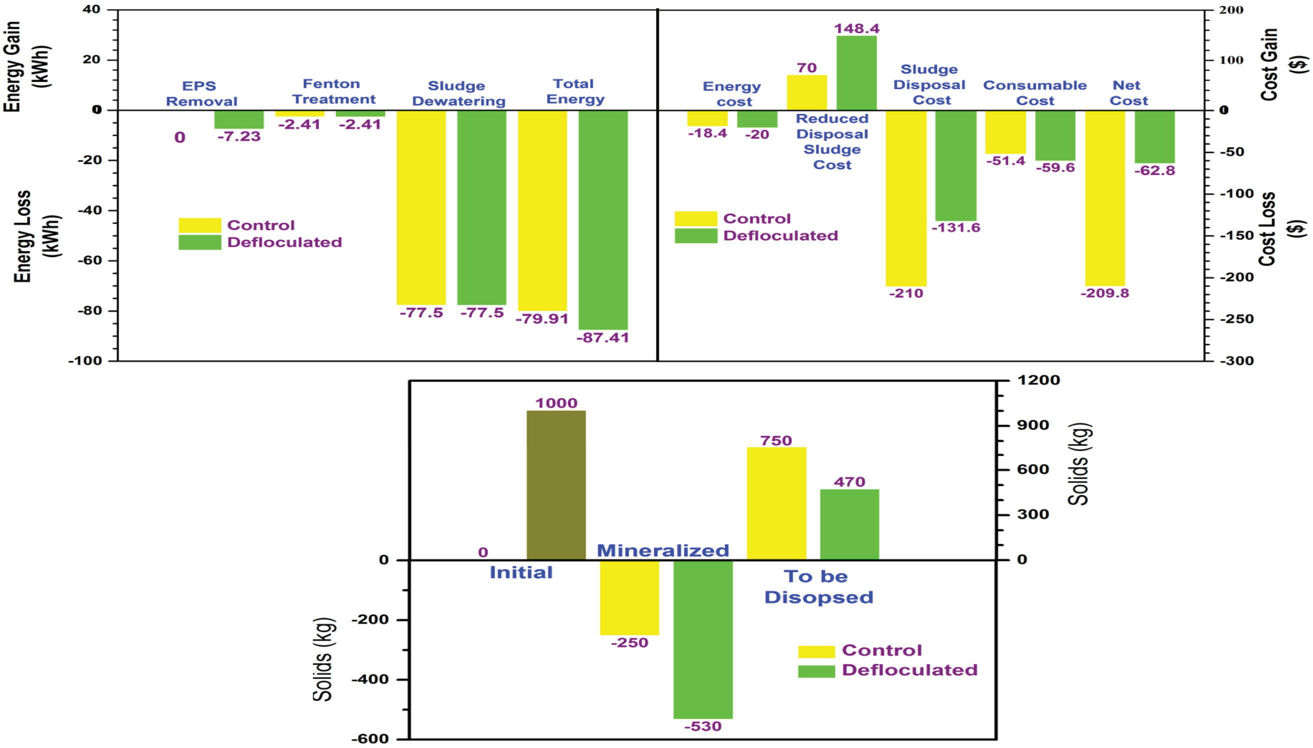

Fig. 6. Economic analysis (per ton TS of sludge).

the results of solids reduction of the present study with other conventional methods like aerobic and anaerobic, maximum solids reduction was achieved by MFP through deflocculation which lowers the net cost of the sludge disposal. Cost benefit was attained by subtracting the cost for SS to be disposed from the total cost. Fig. 6 shows that a net cost of –62.8 and –209.8 USD/ton was achieved for the deflocculated and control, respectively. From the cost analysis it can be concluded that the present method is economically viable.

3.6. The mechanism involved in ZVI catalyzed Fenton process

The whole process was carried out in two steps. The first step of the process is treatment of sludge sample with citric acid that binds with cations for the elimination of EPS to achieve deflocculation as per Eq. (12).

$$\text{Waste activated sludge + citric acid} \rightarrow \text{deflocculated sludge} \quad (12)$$

Further, the deflocculated sample is treated with ZVI and H_2O_2 (modified Fenton reagent) to produce OH and HO_2 radicals which reacts with organics present in the sludge that leads sludge reduction by mineralization process as per Eq. (13).

$$\text{Deflocculated sludge + modified Fenton reagent} \rightarrow \text{sludge reduction (by mineralization process)} \quad (13)$$

Reactions involved with ZVI are shown in Eqs. (14)–(16).

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \text{ (under strongly acidic condition)} \quad (14)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (15)$$

$${}^{\bullet}OH + RH \rightarrow \text{Mineralization of organics} \quad (16)$$

4. Conclusions

Citric acid dosage of 0.06 g/g SS was utilized for the deflocculation of sludge. The outcome of the results proves that the reduction of COD and SS was higher in the deflocculated sludge (76.92% and 52.72%) than the flocculated sludge (38.46% and 25.45%). This shows that the efficiency of the MFP was improved through deflocculation in the sludge treatment process and also kinetic studies reveal that deflocculation faster the rate of the reaction. The VSS study of the MFP indicates the degradation of organics which makes easy of further sludge management process. The present study is relatively economical and easy to operate. It could be concluded that the ZVI is a potential substitute for ferrous salts as a catalyst for the Fenton reaction.

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